Supporting Information

Contents:

1. General Information

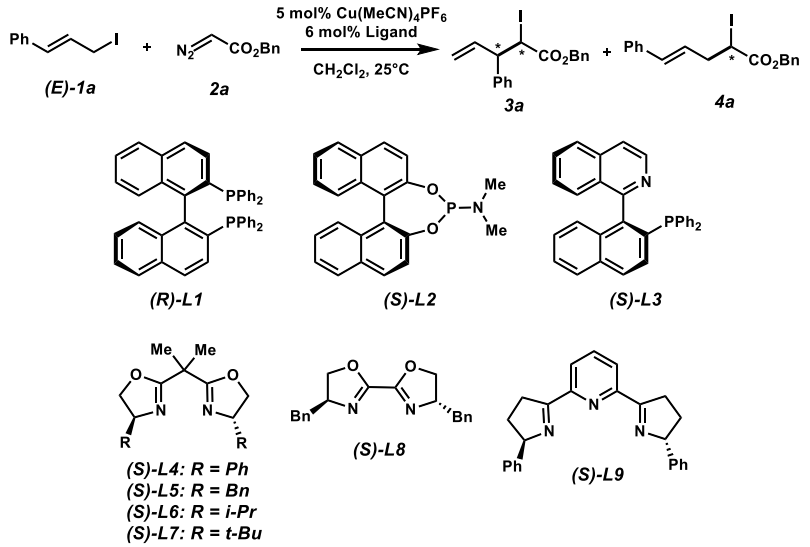
All reactions were carried out in capped reaction vials with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under Argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova-500 spectrometers or Varian Inova-400 spectrometers and ^{13}C NMR spectra were recorded on Varian Inova-400 spectrometers. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) or acetonitrile as an internal standard (1.94 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.0 ppm) or acetonitrile as an internal standard (1.32 ppm) and are reported in terms of chemical shift (δ ppm). Melting points were measured on a Fisher Scientific™ melting point apparatus (12-144). Optical rotations were measured on a JAS DIP-360 digital polarimeter. Infrared spectra were recorded on a Perkin-Elmer 1000 series FTIR. Chiral HPLC analyses were performed on an Agilent 1200 Series system. APCI-LRMS data were measured using an AB Sciex QTRAP-4500 LC/MS. X-Ray Diffraction data was obtained by Dr. Vincent Lynch at the X-ray Diffraction Lab at University of Texas at Austin.

Allylic iodides **1** were synthesized by procedures reported in the literature.[1] Only unreported allylic iodides **1e**, **1g**, **1i–m**, **1t** and **1v–x** have been fully characterized here.

2. Reaction Optimization

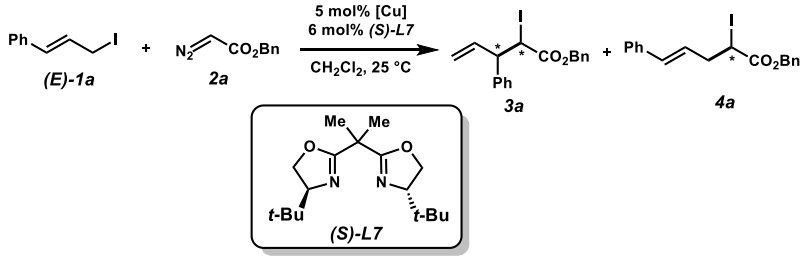
Procedure for Reaction Optimization: An 8 mL reaction vial was charged with copper salt (0.02 mmol) and chiral ligand (0.024 mmol). The vial was then evacuated and refilled with Argon. After dry CH_2Cl_2 (4 mL) was added, the mixture was stirred at 25 ^oC for 2 h. Then the catalyst solution was put into a bath at appropriate temperature, followed by addition of allylic iodide (**1**, 0.4 mmol) and diazo compound **2** (0.42 mmol) in sequence. The mixture was stirred until the reaction was complete (monitored by TLC). The reaction was then concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 20:1) to afford desired rearrangement products as a colorless oil. The regioisomers ratio and diastereoisomers ratio were confirmed by ^1H NMR. The ee values were confirmed by HPLC (when diazo **2a** was utilized, HPLC conditions are Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detecter, t_R= 18.20 min (first diastereoisomer of **3a**), 26.89 min (first diastereoisomer of **3a**), 28.43 min (third diastereoisomer of **3a**), 34.09 min (fourth diastereoisomer of **3a**), 38.70 min (enantioisomer of **4a**) and 42.08 min (enantioisomer of **4a**); when diazo **2b** was utilized, HPLC conditions are Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 220 nm UV detecter, t_R= 8.91 min (first diastereoisomer of **3b**), 9.30 min (second diastereoisomer of **3b**), 19.90 min (third diastereoisomer of **3b**), 21.97 min (fourth diastereoisomer of **3b**), 12.71 min (enantioisomer of **4b**) and 14.18 min (enantioisomer of **4b**)).

Table S1. Reaction optimization: chiral ligands



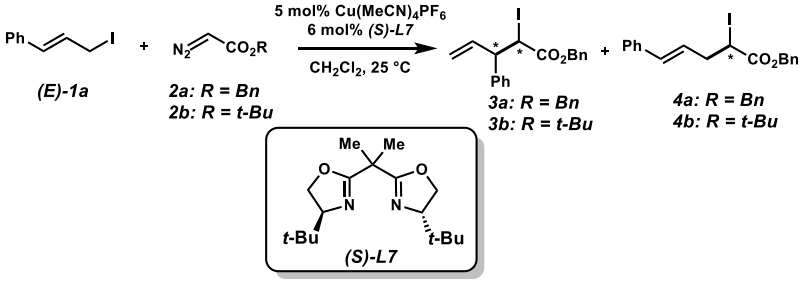
Entry	Ligand	Time	Yield (%)	3 : 4	dr of 3	ee of 3 (%, %)	ee of 4 (%)
1	(*R*)-L1	48 h	19	11 : 89	48 : 52	--, --	0
2	(*S*)-L2 (12 mol%)	48 h	21	18 : 82	58 : 42	69, 31	1
3	(*S*)-L3	48 h	29	<5 : 95	-- : --	--, --	0
4	(*S*)-L4	10 min	62	64 : 36	34 : 66	26, 20	5
5	(*S*)-L5	10 min	71	58 : 42	32 : 68	41, 31	3
6	(*S*)-L6	10 min	73	57 : 43	40 : 60	22, 24	3
7	(S)-L7	10 min	82	87 : 13	45 : 55	75, 81	30
8	(*S*)-L8	10 min	64	65 : 35	36 : 64	2, 25	14
9	(*S*)-L9	24 h	56	56 : 44	37 : 63	42, 12	16

Table S2. Reaction optimization: copper salt



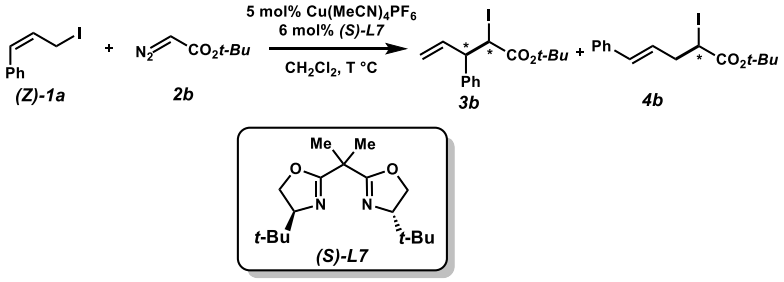
Entry	[Cu]	Time	Yield (%)	3 : 4	dr of 3	ee of 3 (%, %)	ee of 4 (%)
1	$Cu(MeCN)_4PF_6$	10 min	82	87 : 13	45 : 55	75, 81	30
2	CuCl	24 h	63	60 : 40	42 : 58	10, 74	0
3	CuOTf	10 min	57	74 : 26	45 : 55	56, 71	10
4	$Cu(OTf)_2$	10 min	59	75 : 25	45 : 55	59, 71	11

Table S3. Reaction optimization: substrates



Entry	Allyl iodide	Diazo	Time	Yield (%)	3 : 4	dr of 3	ee of 3 (%, %)	ee of 4 (%)
1	*(E)-1a*	*2a*	10 min	82	87 : 13	45 : 55	75, 81	30
2	*(Z)-1a*	*2a*	10 min	80	83 : 17	80 : 20	73, 70	9
3	*(Z)-1a*	*2b*	5 min	85	80 : 20	91 : 9	82, --	--

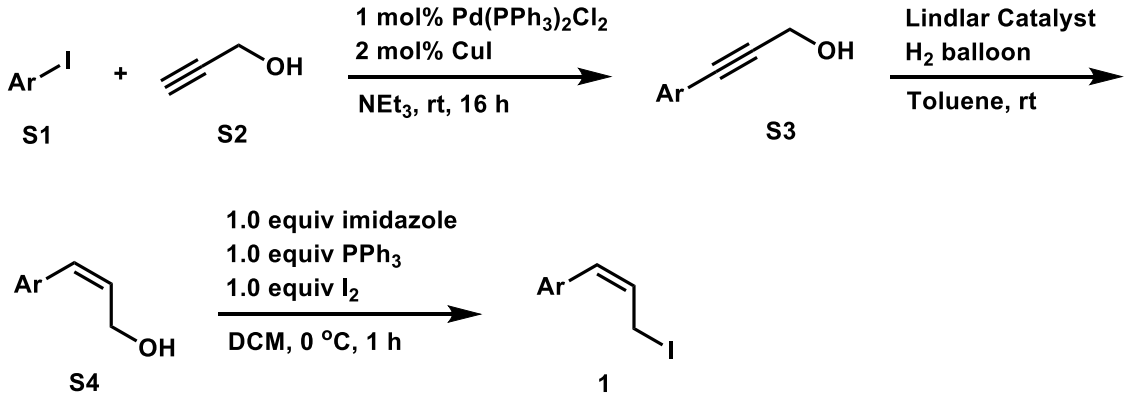
Table S4. Reaction optimization: temperatures



Entry	T (°C)	Time	Yield (%)	3 : 4	dr of 3	ee of 3 (%, %)	ee of 4 (%)
1	*25*	5 min	85	80 : 20	91 : 9	82, --	--
2	*0*	1 h	84	90 : 10	94 : 6	90, --	--
3	*-20*	6 h	82	>95 : 5	>95 : 5	96, --	--

3. Synthesis and Characterization Data for New Allylic Iodides

Typical procedure 3A:

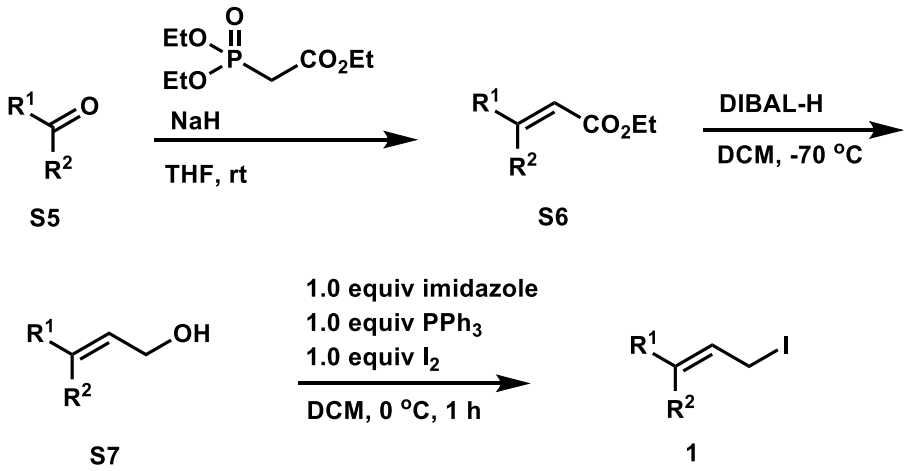


3-Arylprop-2-yn-1-ol, S3: A 100 mL flask was charged with $Pd(PPh_3)Cl_2$ (70 mg, 0.1 mmol) and CuI (38 mg, 0.2 mmol). After the flask was evacuated and refilled with Argon, NEt_3 (20 mL) was added and the suspension was stirred at room temperature. A solution of **S1** (10 mmol) and propargyl alcohol (**S2**, 616 mg, 11 mmol) in NEt_3 (10 mL) was added to the suspension. After the reaction was complete (monitored by TLC), the mixture was filtered through a plug of Celite, which was then washed with EtOAc (20 mL X 3). The combined solution was concentrated and purified by column chromatography on silica (Hexane/EtOAc = 3:1, v/v) to afford desired product **S3** with 78–95% yield.

(*Z*)-3-Arylprop-2-en-1-ol, S4: A 50 mL flash was charged with 3-arylprop-2-yn-1-ol (**S3**, 5 mmol), Lindlar catalyst (250 mg, Aldrich) and toluene (15 mL). After the flask was evacuated and refilled with H_2 by a balloon, the mixture was vigorously stirred at room temperature. After the reaction was complete (monitored by ^1H NMR), the mixture was filtered through a plug of Celite, which was then washed with EtOAc (20 mL X 3). The combined solution was concentrated to afford desired product **S4** with 88–99% yield.

(*Z*)-(3-Iodoprop-1-en-1-yl)arene, 1a–m: A 100 mL flask was charged with PPh_3 (1.31 g, 5 mmol), imidazole (340 mg, 5 mmol) and dichloromethane (15 mL). To the stirring solution was added iodine (1.25 g, 5 mmol) in portions. After 30 minutes, the flask was wrapped in an aluminum foil and placed in an ice bath, followed by slow addition of (*Z*)-3-arylprop-2-en-1-ol (**S4**, 5 mmol, in 10 mL DCM). After the reaction was complete (monitored by TLC), the mixture was filtered through a plug of silica, which was then washed with Hexane/EtOAc (v/v = 10:1, 20 mL X 2). The combined solution was concentrated and purified by flash column chromatography on silica (Hexane/EtOAc = 30:1, v/v) to afford desired product **1a–m** with 70–91% yield.

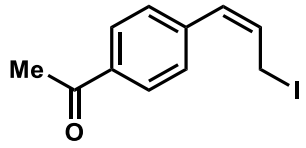
Typical procedure 3B:



Ethyl 3,3-*di*-alkyl-prop-2-enoate, S6[2]: Triethyl phosphonoacetate (10 mmol) was added to a suspension of NaH (10 mmol) in dry THF (50 mL). After 30 min, ketone (**S5**, 8 mmol) in dry THF (10 mL) was added, and the resulting mixture was stirred overnight, and quenched by the addition of water (50 mL). The organic layer was separated, and the aqueous one was extracted with ether (3 × 50 mL). The combined organic solutions were dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica (Hexane/EtOAc = 20:1, v/v) to afford desired product **S6** with 64–88% yield.

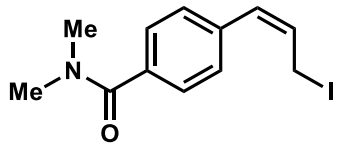
3,3-*di*-Alkyl-prop-2-en-1-ol, S7: To a cooled (−70 °C) solution of the unsaturated ester (**S6**, 5 mmol) in THF (50 mL) was added a DIBAL-H (1.2 M in toluene, 10 mL, 12 mmol). After the reduction was complete (monitored by TLC), the reaction was quenched by the addition of sodium sulfate decahydrate (1.6 g, 5 mmol). The suspension was filtered off and washed with EtOAc (30 mL X 3). The solution was concentrated and purified by column chromatography on silica (dry loading, Hexane/EtOAc = 3:1, v/v) to afford desired product **S7** with 86–96% yield.

1-Iodo-3,3-*di*-Alkyl-prop-2-ene, 1s–x: A 100 mL flask was charged with PPh_3 (1.31 g, 5 mmol), imidazole (340 mg, 5 mmol) and dichloromethane (15 mL). To the stirring solution was added iodine (1.25 g, 5 mmol) in portions. After 30 minutes, the flask was wrapped in an aluminum foil and placed in an ice bath, followed by slow addition of 3,3-*di*-Alkyl-prop-2-en-1-ol (**S7**, 5 mmol, in 10 mL DCM). After the reaction was complete (monitored by TLC), the mixture was filtered through a plug of silica, which was then washed with Pentane/Et_2O (v/v = 10:1, 50 mL). The combined solution was concentrated to afford desired product **1s–x** with 74–90% yield.

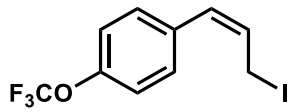


(*Z*)-1-(4-(3-iodoprop-1-en-1-yl)phenyl)ethan-1-one, 1e: A light yellow oil, TLC R_f = 0.40 (Hexane/EtOAc = 6:1, v/v), 76% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.0 Hz, 2H, ArH), 7.43 (d, J = 8.4 Hz, 2H, ArH), 6.44 (d, J = 11.2 Hz, 1H, ArCH=), 6.10 (dt, J_1 = 11.2 Hz and J_2 = 9.2 Hz, 1H, =C<u>H</u>CH_2), 4.04 (d, J = 9.2 Hz, 2H, CH_2I), 2.60 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4 (1C, C=O), 140.4 (1C, ArC), 135.7 (1C, ArC), 130.5 (1C, ArCH=), 130.3 (1C, =$CHCH_2$), 128.6 (2C, ArC), 128.5 (2C, ArC), 26.6 (1C, CH_3), 1.6 (1C, CH_2I). IR (neat): 3018, 2967, 1681, 1356, 1267, 1150, 957, 868, 837

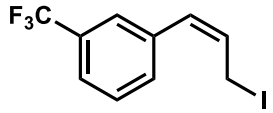
cm^{-1}. APCI-MS calcd for $[C_{11}H_{12}OI, M + H]+$: 286.99, Found 287.00.



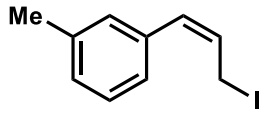
(*Z*)-4-(3-Iodoprop-1-en-1-yl)-*N*,*N*-dimethylbenzamide, 1g: A light yellow oil, TLC R_f = 0.45 (Hexane/EtOAc = 1:2, v/v), 70% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H, ArH), 7.38 (d, *J* = 8.0 Hz, 2H, ArH), 6.43 (d, *J* = 11.5 Hz, 1H, ArCH=), 6.14–5.98 (m, 1H, =C<u>H</u>CH_2), 4.06 (d, *J* = 9.5 Hz, 2H, CH_2I), 3.12 (s, 3H, CH_3), 3.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2 (1C, C=O), 137.0 (1C, ArC), 135.2 (1C, ArC), 130.9 (1C, ArCH=), 129.4 (1C, =$CHCH_2$), 128.4 (2C, ArC), 127.4 (2C, ArC), 39.6 (1C, CH_3), 35.4 (1C, CH_3), 2.0 (1C, CH_2I). IR (neat): 2927, 1631, 1392, 1080, 847, 779 cm^{-1}. APCI-MS calcd for $[C_{12}H_{15}INO, M + H]+$: 316.02, Found 316.02.



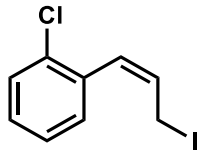
(*Z*)-1-(3-iodoprop-1-en-1-yl)-4-(trifluoromethoxy)benzene, 1i: A light yellow oil, TLC R_f = 0.65 (Hexane/EtOAc = 100:0, v/v), 86% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H, ArH), 7.25 (d, *J* = 8.0 Hz, 2H, ArH), 6.41 (d, *J* = 11.5 Hz, 1H, ArCH=), 6.06 (dt, J_1 = 11.5 Hz and J_2 = 9.0 Hz, 1H, =C<u>H</u>CH2), 4.05 (dd, J_1 = 9.5 Hz and J_2 = 0.5 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2 (q, *J* = 2.0 Hz, 1C, ArC), 134.4 (1C, ArC), 130.3 (1C, ArCH=), 129.9 (2C, ArC), 129.3 (1C, =$CHCH_2$), 121.0 (2C, ArC), 120.4 (q, *J* = 256 Hz, 1C, CF_3), 1.8 (1C, CH_2I). IR (neat): 3022, 1507, 1262, 1210, 1165, 867, 844, 758 cm^{-1}. APCI-MS calcd for $[C_{10}H_9F_3IO, M + H]+$: 328.96, Found 328.97.



(*Z*)-1-(3-Iodoprop-1-en-1-yl)-3-(trifluoromethyl)benzene, 1j: A light yellow oil, TLC R_f = 0.75 (Hexane/EtOAc = 30:1, v/v), 91% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.50 (m, 4H, ArH), 6.45 (d, J = 11.5 Hz, 1H, ArCH=), 6.12 (dt, J_1 = 11.5 Hz and J_2 = 9.0 Hz, 1H, =C<u>H</u>CH_2), 4.03 (dd, J_1 = 9.0 Hz and J_2 = 1.0 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4 (1C, ArC), 131.4 (1C, ArC), 131.0 (q, J = 32.1 Hz, 1C, ArC), 130.2 (1C, ArCH=), 130.1 (1C, ArC), 129.0 (1C, =$CHCH_2$), 125.3 (q, J = 3.8 Hz, 1C, ArC), 124.0 (q, J = 271 Hz, 1C, CF_3), 124.1 (q, J = 3.8 Hz, 1C, ArC), 1.1 (1C, CH_2I). IR (neat): 3022, 1330, 1166, 1126, 1074, 907, 808, 703 cm^{-1}. APCI-MS calcd for [$C_{10}H_9F_3I$, M + H]+: 312.97, Found 312.99.

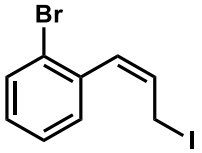


(*Z*)-1-(3-Iodoprop-1-en-1-yl)-3-methylbenzene, 1k: A light yellow oil, TLC R_f = 0.70 (Hexane/EtOAc = 100:0, v/v), 86% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, J = 7.5 Hz, 1H, ArH), 7.21–7.14 (m, 2H, ArH), 7.11 (d, J = 7.5 Hz, 1H, ArH), 6.42 (d, J = 11.0 Hz, 1H, ArCH=), 6.00 (dt, J_1 = 11.0 Hz and J_2 = 9.0 Hz, 1H, =C<u>H</u>CH_2), 4.11 (d, J = 9.0 Hz, 2H, CH_2I), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (1C, ArC), 135.7 (1C, ArC), 132.0 (1C, ArCH=), 129.3 (1C, =$CHCH_2$), 128.4 (1C, ArC), 128.3 (1C, ArC), 128.2 (1C, ArC), 125.5 (1C, ArC), 21.5 (1C, CH_3), 2.9 (1C, CH_2I). IR (neat): 3016, 2918, 1602, 1487, 1149, 913, 798, 755, 699 cm^{-1}. APCI-MS calcd for [$C_{10}H_{12}I$, M + H]+: 259.00, Found 259.00.

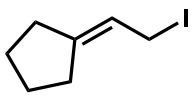


(*Z*)-1-Chloro-2-(3-iodoprop-1-en-1-yl)benzene, 1l: A light yellow oil, TLC R_f = 0.65

(Hexane/EtOAc = 100:0, v/v), 82% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.48 (m, 1H, ArH), 7.45–7.39 (m, 1H, ArH), 7.33 (t, J = 7.5 Hz, 1H, ArH), 7.28–7.22 (m, 1H, ArH), 6.53 (d, J = 11.0 Hz, 1H, ArCH=), 6.14 (dt, J_1 = 11.5 Hz and J_2 = 9.0 Hz, 1H, =C<u>H</u>CH_2), 3.97 (d, J = 9.0 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.9 (1C, ArC), 129.7 (1C, ArC), 129.6 (1C, ArCH=), 129.0 (1C, =$CHCH_2$), 128.9 (1C, ArC), 128.8 (2C, ArC), 126.6 (1C, ArC), 1.8 (1C, CH_2I). IR (neat): 3023, 1589, 1469, 1435, 1147, 1050, 1036, 810, 746, 730 cm^{-1}. APCI-MS calcd for [C_9H_9ClI, M + H]+: 278.94, Found 278.95.

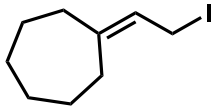


(*Z*)-1-Bomo-2-(3-iodoprop-1-en-1-yl)benzene, 1m: A light yellow oil, TLC R_f = 0.55 (Hexane/EtOAc = 100:0, v/v), 78% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (dd, J_1 = 8.0 Hz and J_2 = 1.0 Hz, 1H, ArH), 7.49 (dd, J_1 = 8.0 Hz and J_2 = 1.0 Hz, 1H, ArH), 7.37 (td, J_1 = 7.5 Hz and J_2 = 0.5 Hz, 1H, ArH), 7.17 (td, J_1 = 8.0 Hz and J_2 = 2.0 Hz, 1H, ArH), 6.47 (d, J = 11.0 Hz, 1H, ArCH=), 6.12 (dt, J_1 = 11.0 Hz and J_2 = 9.0 Hz, 1H, =C<u>H</u>CH_2), 3.95 (dd, J_1 = 9.0 Hz and J_2 = 1.0 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7 (1C, ArC), 132.9 (1C, ArCH=), 131.0 (1C, =$CHCH_2$), 129.4 (1C, ArC), 129.0 (2C, ArC), 127.2 (1C, ArC), 124.2 (1C, ArC), 1.7 (1C, CH_2I). IR (neat): 3052, 3021, 1589, 1466, 1433, 1148, 1025, 808, 765, 746, 723, 666 cm^{-1}. APCI-MS calcd for [C_9H_9BrI, M + H]+: 322.89, Found 322.88.

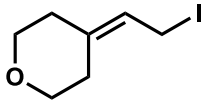


(2-Iodoethylidene)cyclopentane, 1t: A yellow oil, TLC R_f = 0.60 (Hexane/EtOAc = 100:0, v/v), 74% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.67–5.57 (m, 1H, =CH), 3.93 (d, J = 9.0 Hz, 2H, CH_2I), 2.26 (t, J = 7.5 Hz, 2H, CH_2), 2.20 (t, J = 7.5 Hz, 2H, CH_2), 1.76–

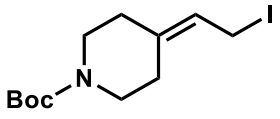
1.68 (m, 2H, CH_2), 1.65–1.58 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1 (1C, =C), 117.6 (1C, =CH), 34.1 (1C, CH_2), 28.3 (1C, CH_2), 26.2 (1C, CH_2), 26.0 (1C, CH_2), 6.2 (1C, CH_2I). IR (neat): 2956, 2867, 1657, 1429, 1142, 854, 668 cm^{-1}. APCI-MS calcd for $[C_7H_{12}I, M + H]+$: 223.00, Found 223.00.



(2-Iodoethylidene)cycloheptane, 1v: A light yellow oil, TLC R_f = 0.80 (Hexane/EtOAc = 100:0, v/v), 90% yield, ^1H NMR (500 MHz, $CDCl_3$): δ 5.53 (t, *J* = 9.0 Hz, 1H, CH=), 3.93 (d, *J* = 8.5 Hz, 2H, CH_2I), 2.28 (t, *J* = 6.0 Hz, 1H, CH_2), 2.20 (t, *J* = 6.0 Hz, 1H, CH_2), 1.68–1.61 (m, 2H, CH_2), 1.57–1.46 (m, 6H, $3CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (1C, C=), 122.0 (1C, =CH), 37.8 (1C, CH_2), 29.8 (1C, CH_2), 29.6 (1C, CH_2), 29.1 (1C, CH_2), 28.6 (1C, CH_2), 26.0 (1C, CH_2), 4.4 (1C, CH_2I). IR (neat): 2923, 2850, 1632, 1451, 1441, 1142, 955, 833 cm^{-1}. APCI-MS calcd for $[C_9H_{16}I_3, M + H]+$: 251.03, Found 251.03.

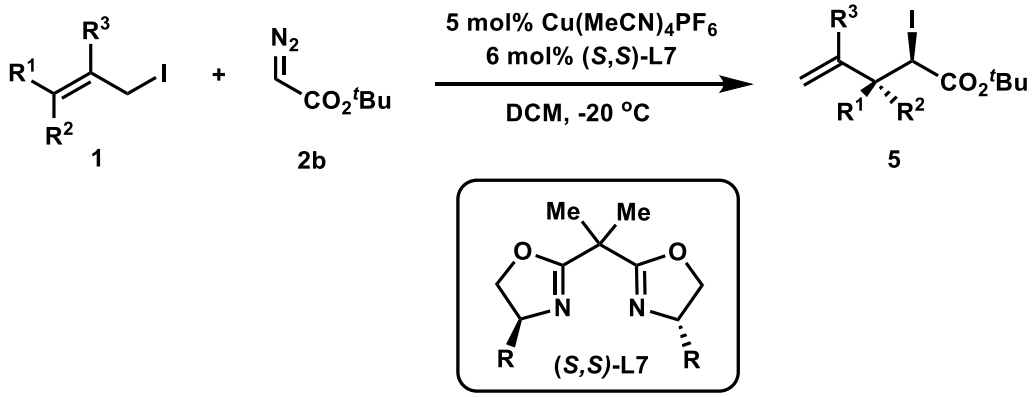


4-(2-Iodoethylidene)tetrahydro-2H-pyran, 1w: A light yellow oil, TLC R_f = 0.40 (Hexane/EtOAc = 10:1, v/v), 82% yield, ^1H NMR (400 MHz, $CDCl_3$): δ 5.58 (t, *J* = 9.2 Hz, 1H, =CH), 3.91 (d, *J* = 8.4 Hz, 2H, CH_2I), 3.70–3.62 (m, 4H, $2CH_2O$), 2.31–2.25 (m, 2H, CH_2), 2.24–2.18 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (1C, C=), 120.6 (1C, =CH), 68.9 (1C, CH_2O), 67.6 (1C, CH_2O), 36.6 (1C, CH_2), 29.3 (1C, CH_2), 1.3 (1C, CH_2I). IR (neat): 2958, 2846, 1656, 1230, 1146, 1098, 986, 852, 831, 660 cm^{-1}. APCI-MS calcd for $[C_7H_{12}IO, M + H]+$: 238.99, Found 238.99.



***tert*-Butyl 4-(2-iodoethylidene)piperidine-1-carboxylate, 1x:** A light yellow oil, TLC Rf = 0.40 (Hexane/EtOAc = 4:1, v/v), 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62 (t, *J* = 8.5 Hz, 1H, =CH), 3.91 (d, *J* = 8.5 Hz, 2H, CH_2I), 3.48–3.36 (m, 4H, $2CH_2N$), 2.28–2.12 (m, 4H, $2CH_2$), 1.46 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (1C, C=O), 141.3 (1C, C=), 121.3 (1C, =CH), 79.7 (1C, $O\underline{C}(CH_3)_3$), 35.6 (2C, $2CH_2N$), 28.4 (3C, $OC(\underline{C}H_3)_3$), 28.0 (2C, $2CH_2$), 1.2 (1C, CH_2I). IR (neat): 2975, 2935, 1694, 1422, 1365, 1234, 1169, 1117, 984, 864, 769 cm^{-1}. APCI-MS calcd for $[C_{12}H_{21}INO_2, M + H]+$: 338.06, Found 338.06.

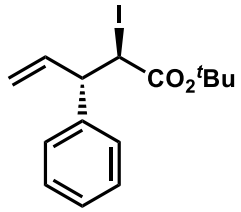
4. Typical Procedure for Enantioselective [2,3]-Rearrangements



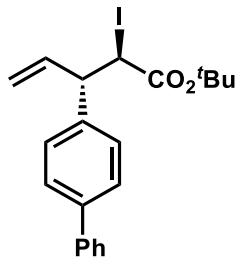
An 8 mL reaction vial was charged with $[Cu(MeCN)_4]PF_6$ (7.4 mg, 0.02 mmol) and (*S*,*S*)-L7 (7.2 mg, 0.024 mmol). The vial was then evacuated and refilled with Argon. After dry CH_2Cl_2 (4 mL) was added, the mixture was stirred at 23 °C for 2 h. Then the catalyst solution was cooled to –20 °C, followed by addition of allylic iodide (**1**, 0.4 mmol) and **2b** (0.42 mmol) in sequence. The mixture was stirred at –20 °C until the reaction was complete (monitored by TLC, about 6 h). The reaction was then

concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 30:1) to afford [2,3]-rearrangement products.

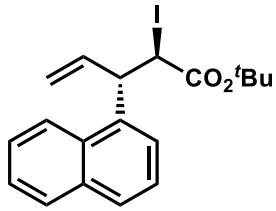
5. Characterization Data for [2,3]-Rearrangement Products



(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-phenylpent-4-enoate, 5a: Colorless semi-oil, TLC R_f = 0.58 (Hexane/EtOAc = 30:1, v/v), 82% yield, regioisomers ratio > 95:5, *anti* / *syn* > 95 : 5, 96% ee. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 220 nm UV detecter, t_R= 8.91 min (minor) and t_R= 9.30 min (major). $[\alpha]_D^{23}$ +31.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.27 (m, 2H, ArH), 7.24–7.20 (m, 1H, ArH), 7.20–7.16 (m, 2H, ArH), 6.02–5.92 (m, 1H, =CH), 5.18 (d, *J* = 10.5 Hz, 1H, 1/2(=CH_2)), 5.12 (d, *J* = 17.0 Hz, 1H, 1/2(=CH_2)), 4.48 (d, *J* = 11.5 Hz, 1H, CHI), 3.84 (dd, J_1 = 11.5 Hz and J_2 = 8.5 Hz, 1H, ArCH), 1.19 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, C=O), 139.6 (1C, ArC), 139.0 (1C, =CH), 128.6 (2C, ArC), 127.9 (2C, ArC), 127.3 (1C, ArC), 117.8 (1C, =CH_2), 81.9 (1C, O$\underline{C}(CH_3)_3$), 54.6 (1C, ArCH), 29.1 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2977, 1728, 1368, 1272, 1155, 918, 847, 699 cm^{-1}. APCI-MS calcd for [$C_{15}H_{20}IO_2$, M + H]$^+$: 359.05, Found 359.05.

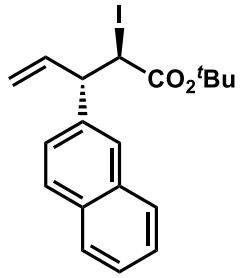


(+)-*tert*-Butyl (2*R*, 3*S*)-3-([1,1'-biphenyl]-4-yl)-2-iodopent-4-enoate, 5b: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 30:1, v/v), 78% yield, regioisomers ratio > 95:5, *anti* / *syn* = 88 : 12, 95% ee. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm UV detecter, t_R= 13.71 min (major) and t_R= 16.82 min (minor). $[\alpha]_D^{23}$ +32.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.50 (m, 4H, ArH), 7.46–7.40 (m, 2H, ArH), 7.37–7.32 (m, 1H, ArH), 7.27 (d, *J* = 8.5 Hz, 2H, ArH), 6.06–5.94 (m, 1H, =CH), 5.22 (d, *J* = 10.0 Hz, 1H, 1/2(=CH_2)), 5.17 (d, *J* = 16.5 Hz, 1H, 1/2(=CH_2)), 4.51 (d, *J* = 11.5 Hz, 1H, CHI), 3.90 (dd, J_1 = 11.5 Hz and J_2 = 8.5 Hz, 1H, ArCH), 1.21 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (1C, C=O), 140.6 (1C, ArC), 140.2 (1C, ArC), 138.9 (1C, =CH), 138.7 (1C, ArC), 128.8 (2C, ArC), 128.3 (2C, ArC), 127.3 (1C, ArC), 127.2 (2C, ArC), 127.0 (2C, ArC), 117.9 (1C, =CH_2), 82.0 (1C, O$\underline{C}(CH_3)_3$), 54.2 (1C, ArCH), 29.0 (1C, CHI), 27.3 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2977, 2928, 1728, 1486, 1368, 1272, 1156, 919, 840, 763, 697 cm^{-1}. APCI-MS calcd for $[C_{21}H_{24}IO_2, M + H]^+$: 435.08, Found 435.08.



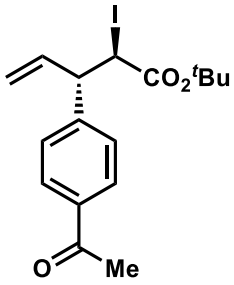
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(naphthalen-1-yl)pent-4-enoate, 5c: Colorless semi-oil, TLC R_f = 0.50 (Hexane/EtOAc = 30:1, v/v), 93% yield, regioisomers ratio > 95:5, *anti* / *syn* > 95 : 5, 90% ee (ee value was determined by derivatization to compound **6c**). $[\alpha]_D^{24}$ +7.2 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_3CN): δ 8.26 (d, *J* = 8.5 Hz, 1H,

ArH), 7.92 (d, J = 8.5 Hz, 1H, ArH), 7.81 (d, J = 7.5 Hz, 1H, ArH), 7.62–7.52 (m, 2H, ArH), 7.52–7.45 (m, 2H, ArH), 6.11–6.00 (m, 1H, =CH), 5.27–5.21 (m, 1H, 1/2(=CH_2)), 5.18–5.13 (m, 1H, 1/2(=CH_2)), 4.93 (d, J = 11.5 Hz, 1H, CHI), 4.75 (dd, J_1 = 11.5 Hz and J_2 = 9.0 Hz, 1H, ArCH), 0.95 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, CD_3CN): δ 170.0 (1C, C=O), 140.0 (1C, =CH), 137.9 (1C, ArC), 134.9 (1C, ArC), 131.9 (1C, ArC), 129.7 (1C, ArC), 128.6 (1C, ArC), 127.3 (1C, ArC), 126.9 (1C, ArC), 126.3 (1C, ArC), 124.8 (1C, ArC), 124.4 (1C, ArC), 118.2 (1C, =CH_2), 82.3 (1C, O<u>C</u>$(CH_3)_3$), 49.9 (1C, ArCH), 30.2 (1C, CHI), 27.2 (3C, OC(<u>C</u>$H_3)_3$). IR (neat): 2978, 2931, 1726, 1368, 1278, 1156, 920, 842, 779 cm^{-1}. APCI-MS calcd for $[C_{19}H_{22}IO_2, M + H]^+$: 409.07, Found 409.07.

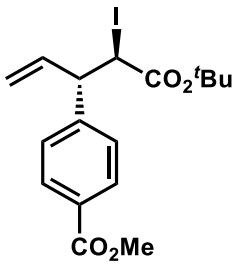


(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(naphthalen-2-yl)pent-4-enoate, 5d: Colorless semi-oil, TLC R_f = 0.55 (Hexane/EtOAc = 30:1, v/v), 77% yield, regioisomers ratio > 95:5, *anti* / *syn* = 93 : 7, 96% ee (ee value was determined by derivatization to compound **6d**). $[\alpha]_D^{24}$ +45.0 (*c* 0.60, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.76 (m, 3H, ArH), 7.66 (s, 1H, ArH), 7.49–7.43 (m, 2H, ArH), 7.33 (dd, J_1 = 8.5 Hz and J_2 = 1.5 Hz, 1H, ArH), 6.12–6.02 (m, 1H, =CH), 5.23 (d, J = 10.0 Hz, 1H, 1/2(=CH_2)), 5.17 (d, J = 17.0 Hz, 1H, 1/2(=CH_2)), 4.62 (d, J = 11.5 Hz, 1H, CHI), 4.04 (dd, J_1 = 11.5 Hz and J_2 = 8.5 Hz, 1H, ArCH), 1.14 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, <u>C</u>$O_2C(CH_3)_3$), 139.0 (1C, CH=), 137.1 (1C, ArC), 133.3 (1C, ArC), 132.5 (1C, ArC), 128.3 (1C, ArC), 127.7 (1C, ArC), 127.6 (1C, ArC), 126.7 (1C, ArC), 126.2 (1C, ArC), 125.9 (1C, ArC), 125.8 (1C, ArC), 118.0 (1C, =CH_2), 81.9 (1C, O<u>C</u>$(CH_3)_3$), 54.4 (1C, ArCH), 29.1 (1C, CHI), 27.2 (3C, OC(<u>C</u>$H_3)_3$). IR (neat): 2978, 2932, 1728, 1369, 1276, 1155, 922, 843, 818, 745, 616 cm^{-1}. APCI-MS calcd for $[C_{19}H_{22}IO_2, M + H]^+$: 409.07,

Found 409.07.

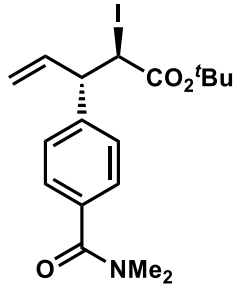


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-acetylphenyl)-2-iodopent-4-enoate, 5e: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 1:1, v/v), 75% yield, regioisomers ratio > 95:5, *anti* / *syn* = 92 : 8, 96% ee. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm UV detecter, t_R= 16.70 min (major) and t_R= 21.45 min (minor). $[\alpha]_D^{25}$ +34.0 (*c* 0.60, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2H, ArH), 7.30 (d, *J* = 8.0 Hz, 2H, ArH), 6.00–5.87 (m, 1H, =CH), 5.21 (d, *J* = 10.0 Hz, 1H, 1/2(=CH_2)), 5.12 (d, *J* = 17.0 Hz, 1H, 1/2(=CH_2)), 4.50 (d, *J* = 11.5 Hz, 1H, CHI), 3.92 (dd, J_1 = 11.5 Hz and J_2 = 9.0 Hz, 1H, ArCH), 2.58 (s, 3H, $COCH_3$), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6 (1C, $\underline{C}OCH_3$), 168.8 (1C, $\underline{C}O_2C(CH_3)_3$), 145.2 (1C, ArC), 138.3 (1C, =CH), 136.1 (1C, ArC), 128.7 (2C, ArC), 128.1 (2C, ArC), 118.5 (1C, =CH_2), 82.2 (1C, O$\underline{C}(CH_3)_3$), 54.4 (1C, ArCH), 28.1 (1C, CHI), 27.3 (3C, OC($\underline{C}H_3)_3$), 26.6 (1C, CO$\underline{C}H_3$). IR (neat): 2978, 2928, 1727, 1684, 1368, 1268, 1157, 958, 839 cm^{-1}. APCI-MS calcd for [$C_{17}H_{22}IO_3$, M + H]+: 401.06, Found 401.06.



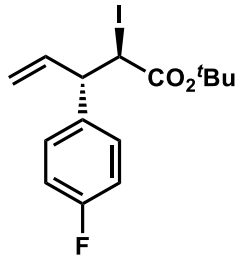
(+)-Methyl 4-((3*S*, 4*R*)-5-(*tert*-butoxy)-4-iodo-5-oxopent-1-en-3-yl)benzoate, 5f:

Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 10:1, v/v), 75% yield, regioisomers ratio = 93:7, *anti* / *syn* = 94 : 6, 93% ee. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 97:3, 0.5 mL/min, 220 nm UV detecter, t_R= 15.41 min (major) and t_R= 16.77 min (minor). $[\alpha]_D^{23}$ +18.7 (*c* 0.60, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.5 Hz, 2H, ArH), 7.27 (d, *J* = 8.5 Hz, 2H, ArH), 6.00–5.90 (m, 1H, =CH), 5.21 (d, *J* = 10.0 Hz, 1H, 1/2(=CH_2)), 5.11 (d, *J* = 17.0 Hz, 1H, 1/2(=CH_2)), 4.49 (d, *J* = 11.5 Hz, 1H, CHI), 3.91–3.88 (m, 4H, ArCH & OCH_3), 1.19 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (1C, $\underline{C}O_2C(CH_3)_3$), 166.7 (1C, $\underline{C}O_2CH_3$), 144.9 (1C, ArC), 138.3 (1C, CH=), 129.9 (2C, ArC), 129.1 (1C, ArC), 127.9 (2C, ArC), 118.5 (1C, =CH_2), 82.2 (1C, O$\underline{C}(CH_3)_3$), 54.4 (1C, ArCH), 52.1 (1C, OCH_3), 28.1 (1C, CHI), 27.3 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2978, 2949, 1724, 1608, 1435, 1369, 1280, 1157, 1114, 766, 709 cm^{-1}. APCI-MS calcd for $[C_{17}H_{22}IO_4, M + H]^+$: 417.06, Found 417.06.

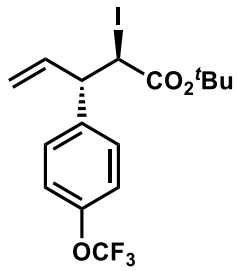


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-(dimethylcarbamoyl)phenyl)-2-iodopent-4-enoate, 5g: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 1:2, v/v), 63% yield, regioisomers ratio > 95:5, *anti* / *syn* = 94 : 6, 94% ee. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 94:6, 0.5 mL/min, 220 nm UV detecter, t_R= 21.10 min (major) and t_R= 22.95 min (minor). $[\alpha]_D^{25}$ +32.7 (*c* 0.30, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.0 Hz, 2H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 6.00–5.88 (m, 1H, =CH), 5.19 (d, *J* = 10.0 Hz, 1H, 1/2(=CH_2)), 5.11 (d, *J* = 17.0 Hz, 1H, 1/2(=CH_2)), 4.47 (d, *J* = 11.5 Hz, 1H, CHI), 3.87 (dd, J_1 = 11.5 Hz and J_2 = 8.0 Hz, 1H, ArCH), 3.09 (s, 3H, NCH_3), 2.93 (s, 3H, NCH_3), 1.21 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100

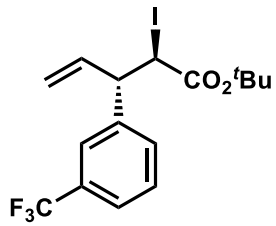
MHz, $CDCl_3$): δ 171.1 (1C, $\underline{C}ON(CH_3)_2$), 168.9 (1C, $\underline{C}O_2C(CH_3)_3$), 141.2 (1C, ArC), 138.6 (1C, =CH), 135.3 (1C, ArC), 127.9 (2C, ArC), 127.5 (2C, ArC), 118.2 (1C, $=CH_2$), 82.1 (1C, $O\underline{C}(CH_3)_3$), 54.2 (1C, ArCH), 39.5 (1C, NCH_3), 35.3 (1C, NCH_3), 28.5 (1C, CHI), 27.3 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2978, 1727, 1634, 1393, 1270, 1157, 1081, 856 cm^{-1}. APCI-MS calcd for $[C_{18}H_{25}INO_3$, M + H]+: 430.09, Found 430.09.



(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-fluorophenyl)-2-iodopent-4-enoate, 5h: Colorless semi-oil, TLC R_f = 0.55 (Hexane/EtOAc = 30:1, v/v), 82% yield, regioisomers ratio = 94:6, *anti* / *syn* = 93 : 7, 93% ee (ee value was determined by transformation to **6h**). $[\alpha]_D^{23}$ +14.0 (*c* 0.40, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 7.19–7.12 (m, 2H, ArH), 7.02–6.95 (m, 2H, ArH), 6.00–5.90 (m, 1H, =CH), 5.19 (d, *J* = 10.5 Hz, 1H, 1/2(=CH2)), 5.09 (d, *J* = 17.0 Hz, 1H, 1/2(=CH2)), 4.41 (d, *J* = 11.5 Hz, 1H, CHI), 3.84 (dd, J_1 = 11.5 Hz and J_2 = 8.5 Hz, 1H, ArCH), 1.22 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, C=O), 161.9 (d, *J* = 244.9 Hz, 1C, C–F), 138.8 (1C, ArC), 135.3 (d, *J* = 3.3 Hz, 1C, =CH), 129.5 (d, *J* = 7.9 Hz, 2C, ArC), 118.0 (2C, ArC), 115.5 (d, *J* = 21.3 Hz, 1C, $=CH_2$), 82.0 (1C, $O\underline{C}(CH_3)_3$), 53.6 (1C, ArCH), 28.7 (1C, CHI), 27.3 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2978, 2931, 1726, 1602, 1508, 1368, 1259, 1229, 1157, 1124, 834, 784 cm^{-1}. APCI-MS calcd for $[C_{15}H_{19}FIO_2$, M + H]$^+$: 377.04, Found 377.04.

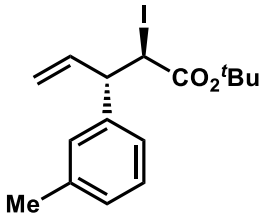


(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(4-(trifluoromethoxy)phenyl)pent-4-enoate, 5i: Colorless semi-oil, TLC R_f = 0.65 (Hexane/EtOAc = 30:1, v/v), 78% yield, regioisomers ratio > 95:5, *anti* / *syn* = 92 : 8, 93% ee (ee value was determined by transformation to **6i**). $[\alpha]_D^{25}$ +21.5 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.21 (m, 2H, ArH), 7.18–7.13 (m, 2H, ArH), 6.00–5.90 (m, 1H, =CH), 5.21 (d, *J* = 10.0 Hz, 1H, 1/2(=CH_2)), 5.12 (d, *J* = 17.0 Hz, 1H, 1/2(=CH_2)), 4.42 (d, *J* = 11.5 Hz, 1H, CHI), 3.87 (dd, J_1 = 11.5 Hz and J_2 = 8.5 Hz, 1H, ArCH), 1.19 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8 (1C, C=O), 148.3 (q, *J* = 2.1 Hz, 1C, ArC), 138.4 (1C, ArC), 138.3 (1C, =CH), 129.3 (2C, ArC), 121.2 (2C, ArC), 120.4 (q, *J* = 256 Hz, 1C, CF_3), 118.3 (1C, =CH_2), 82.2 (1C, O$\underline{C}(CH_3)_3$), 53.8 (1C, ArCH), 28.3 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2981, 2934, 1728, 1508, 1370, 1264, 1222, 1163, 1125, 922, 846 cm^{-1}. APCI-MS calcd for [$C_{16}H_{19}F_3IO_3$, M + H]+: 443.03, Found 443.03.

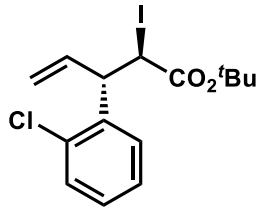


(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(3-(trifluoromethyl)phenyl)pent-4-enoate, 5j: Colorless semi-oil, TLC R_f = 0.50 (Hexane/EtOAc = 30:1, v/v), 72% yield, regioisomers ratio > 95:5, *anti* / *syn* = 94 : 6, 97% ee (ee value was determined by transformation to **6j**). $[\alpha]_D^{25}$ +21.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–7.48 (m, 1H, ArH), 7.46–7.37 (m, 3H, ArH), 6.03–5.91 (m, 1H, =CH), 5.24 (d, *J* = 10.5 Hz, 1H, 1/2(=CH_2)), 5.14 (d, *J* = 16.5 Hz, 1H, 1/2(=CH_2)), 4.47 (d, *J* = 11.5 Hz, 1H, CHI), 3.92 (dd, J_1 = 11.0

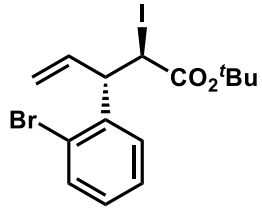
Hz and J_2 = 8.5 Hz, 1H, ArCH), 1.19 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (1C, C=O), 140.7 (1C, ArC), 138.1 (1C, =CH), 131.3 (1C, ArC), 130.9 (q, J = 32.3 Hz, 1C, ArC), 129.1 (1C, ArC), 124.8 (q, J = 3.7 Hz, 1C, ArC), 124.2 (q, J = 3.8 Hz, 1C, ArC), 123.9 (q, J = 271 Hz, 1C, CF_3), 118.7 (1C, $=CH_2$), 82.3 (1C, $O\underline{C}(CH_3)_3$), 54.2 (1C, ArCH), 28.0 (1C, CHI), 27.2 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2981, 2933, 1727, 1370, 1330, 1274, 1164, 1128, 1074, 704 cm^{-1}. APCI-MS calcd for $[C_{16}H_{19}F_3IO_2$, M + H]+: 427.04, Found 427.04.



(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(*m*-tolyl)pent-4-enoate, 5k: Colorless oil, TLC R_f = 0.65 (Hexane/EtOAc = 30:1, v/v), 87% yield, regioisomers ratio > 95:5, *anti* / *syn* = 95 : 5, 94% ee (ee value was determined by transformation to **6k**). $[\alpha]_D^{25}$ +30.0 (*c* 0.50, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 7.18 (t, J = 7.5 Hz, 1H, ArH), 7.03 (d, J = 7.5 Hz, 1H, ArH), 7.00–6.96 (m, 2H, ArH), 6.00–5.90 (m, 1H, =CH), 5.17 (d, J = 10.0 Hz, 1H, 1/2(=CH_2)), 5.12 (d, J = 17.0 Hz, 1H, 1/2(=CH_2)), 4.46 (d, J = 11.5 Hz, 1H, CHI), 3.80 (dd, J_1 = 11.5 Hz and J_2 = 9 .0 Hz, 1H, ArCH), 2.31 (s, 3H, CH_3), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, C=O), 139.5 (1C, ArC), 139.1 (1C, ArC), 138.2 (1C, =CH), 128.7 (1C, ArC), 128.5 (1C, ArC), 128.0 (1C, ArC), 124.7 (1C, ArC), 117.6 (1C, $=CH_2$), 81.8 (1C, $O\underline{C}(CH_3)_3$), 54.6 (1C, ArCH), 29.3 (1C, CHI), 27.3 (3C, $OC(\underline{C}H_3)_3$), 21.4 (1C, CH_3). IR (neat): 2978, 2929, 1729, 1368, 1274, 1154, 1122, 920, 844, 769, 704 cm^{-1}. APCI-MS calcd for $[C_{16}H_{22}IO_2$, M + H]+: 373.07, Found 373.07.

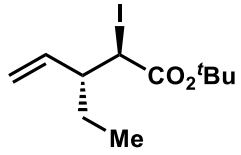


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-chlorophenyl)-2-iodopent-4-enoate, 5l: Colorless oil, TLC R_f = 0.60 (Hexane/EtOAc = 30:1, v/v), 64% yield, regioisomers ratio = 88:12, *anti* / *syn* > 95 : 5, 95% ee (ee value was determined by transformation to **6l**). $[\alpha]_D^{25}$ +26.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.5 Hz, 1H, ArH), 7.26–7.14 (m, 3H, ArH), 5.97–5.86 (m, 1H, =CH), 5.23–5.11 (m, 2H, =CH_2), 4.63 (d, *J* = 11.5 Hz, 1H, CHI), 4.47–4.37 (m, 1H, ArCH), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (1C, C=O), 137.5 (1C, ArC), 137.3 (1C, =CH), 133.7 (1C, ArC), 130.0 (1C, ArC), 128.3 (1C, ArC), 127.9 (1C, ArC), 127.0 (1C, ArC), 118.5 (1C, =CH_2), 82.1 (1C, O$\underline{C}(CH_3)_3$), 50.4 (1C, ArCH), 28.0 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2980, 1728, 1474, 1369, 1276, 1158, 1035,924, 847, 754 cm^{-1}. APCI-MS calcd for $[C_{15}H_{19}ClIO_2$, M + H]+: 393.01, Found 393.01.

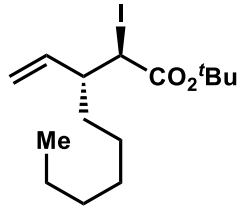


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-bromophenyl)-2-iodopent-4-enoate, 5m: Colorless oil, TLC R_f = 0.55 (Hexane/EtOAc = 30:1, v/v), 56% yield, regioisomers ratio = 82:18, *anti* / *syn* > 95 : 5, 95% ee (ee value was determined by transformation to **6m**). $[\alpha]_D^{25}$ +22.5 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (dd, J_1 = 8.0 Hz and J_2 = 1.0 Hz, 1H, ArH), 7.20–7.26 (m, 1H, ArH), 7.18 (dd, J_1 = 8.0 Hz and J_2 = 1.5 Hz, 1H, ArH), 7.11–7.05 (m, 1H, ArH), 5.94–5.82 (m, 1H, =CH), 5.23–5.13 (m, 2H, =CH_2), 4.62 (d, *J* = 11.5 Hz, 1H, CHI), 4.46–4.36 (m, 1H, ArCH), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 168.6 (1C, C=O), 139.1 (1C, ArC), 137.2 (1C, =CH), 133.3 (1C, ArC), 128.5 (1C, ArC), 127.8 (1C, ArC), 127.6 (1C, ArC), 124.5 (1C, ArC), 118.5 (1C, $=CH_2$), 82.1 (1C, $O\underline{C}(CH_3)_3$), 52.7 (1C, ArCH), 28.1 (1C, CHI), 27.2 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2979, 1726, 1470, 1369, 1277, 1157, 1024, 924, 846, 753 cm^{-1}. APCI-MS calcd for $[C_{15}H_{19}BrIO_2, M + H]+$: 436.96, Found 436.96.

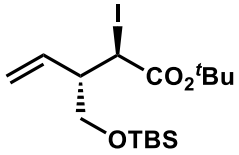


(+)-*tert*-Butyl (2*R*, 3*R*)-3-ethyl-2-iodopent-4-enoate, 5n: Colorless semi-oil, TLC R_f = 0.70 (Hexane/EtOAc = 30:1, v/v), 72% yield, regioisomers ratio = >95 : 5, *anti* / *syn* = 94 : 6, 93% ee (ee value was determined by transformation to compound **6n**). $[\alpha]_D^{24}$ +21.6 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.51–5.43 (m, 1H, CH=), 5.18 (dd, J_1 = 10.0 Hz and J_2 = 1.5 Hz, 1H, 1/2(=CH_2)), 5.09 (dq, J_1 = 17.0 Hz and J_2 = 1.0 Hz, 1H, 1/2(=CH_2)), 4.14 (d, J = 9.0 Hz, 1H, CHI), 2.32 (qd, J_1 = 9.0 Hz and J_2 = 4.0 Hz, 1H, CH), 1.57–1.51 (m, 1H, 1/2CH_2), 1.46 (s, 9H, $C(CH_3)_3$), 1.35–1.28 (m, 1H, 1/2CH_2), 0.90 (d, J = 7.5 Hz, 1H, CHI); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5 (1C, C=O), 139.0 (1C, =CH), 118.0 (1C, $=CH_2$), 82.1 (1C, $O\underline{C}(CH_3)_3$), 49.5 (1C, CH), 31.6 (1C, CHI), 27.6 (3C, $OC(\underline{C}H_3)_3$), 25.8 (1C, CH_2), 12.0 (1C, CH_3). IR (neat): 2971, 2932, 1731, 1369, 1260, 1166, 1128, 919, 804 cm^{-1}. APCI-MS calcd for $[C_{11}H_{20}IO_2, M + H]^+$: 311.05, Found 311.05.

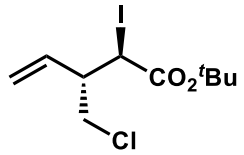


(+)-*tert*-Butyl (2*R*, 3*R*)-2-iodo-3-vinylnonanoate, 5o: Colorless semi-oil, TLC R_f = 0.75 (Hexane/EtOAc = 30:1, v/v), 78% yield, regioisomers ratio = >95:5, *anti* / *syn* = 93 : 7,

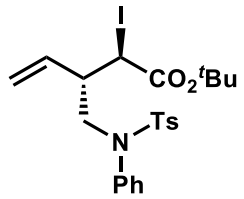
91% ee (ee value was determined by transformation to compound **6o**). $[\alpha]_D^{24}$ +21.6 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.58–5.41 (m, 1H, CH=), 5.16 (dd, J_1 = 10.5 Hz and J_2 = 2.0 Hz, 1H, 1/2(=CH_2)), 5.10–5.04 (m, 1H, 1/2(=CH_2)), 4.11 (d, J = 9.5 Hz, 1H, CHI), 2.45–2.36 (m, 1H, CH), 1.46 (s, 9H, $C(CH_3)_3$), 1.37–1.17 (m, 10H, 5CH2), 0.86 (*t*, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5 (1C, C=O), 139.3 (1C, =CH), 117.8 (1C, =CH_2), 82.0 (1C, $OC(CH_3)_3$), 47.9 (1C, CHI), 32.7 (1C, CH), 31.9 (1C, CH_2), 31.6 (1C, CH_2), 29.0 (1C, CH_2), 27.6 (3C, $OC(\underline{C}H_3)_3$), 27.3 (1C, CH_2), 22.6 (1C, CH_2), 14.0 (1C, CH_3). IR (neat): 2930, 2857, 1731, 1369, 1275, 1160, 1128, 918, 845 cm^{-1}. APCI-MS calcd for $[C_{15}H_{28}IO_2, M + H]^+$: 367.11, Found 367.14.



(+)-*tert*-Butyl (2*R*, 3*S*)-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-iodopent-4-enoate, 5p: Colorless semi-oil, TLC R_f = 0.80 (Hexane/EtOAc = 30:1, v/v), 82% yield, regioisomers ratio = >95:5, *anti* / *syn* > 95 : 5, 92% ee (ee value was determined by transformation to compound **6p**). $[\alpha]_D^{24}$ +40.7 (*c* 0.60, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77–5.68 (m, 1H, =CH), 5.21–5.12 (m, 2H, =CH_2), 4.59 (d, J = 7.5 Hz, 1H, CHI), 3.71–3.67 (m, 1H, 1/2(CH_2O)), 3.54–3.49 (m, 1H, 1/2(CH_2O)), 2.46–2.39 (m, 1H, CH), 1.46 (s, 9H, $OC(CH_3)_3$), 0.89 (s, 9H, $SiC(CH_3)_3$), 0.05 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9 (1C, C=O), 133.2 (1C, CH=), 126.5 (1C, CH=), 81.9 (1C, $O\underline{C}(CH_3)_3$), 63.2 (1C, OCH_2), 38.9 (1C, CHI), 27.6 (3C, $OC(\underline{C}H_3)_3$), 25.9 (3C, $SiC(\underline{C}H_3)_3$), 22.1 (1C, CH_2), 18.4 (1C, $Si\underline{C}(CH_3)_3$), –5.2 (2C, $Si(CH_3)_2$). IR (neat): 2956, 2930, 2858, 1729, 1472, 1369, 1257, 1164, 1104, 837, 777 cm^{-1}. APCI-MS calcd for $[C_{16}H_{32}IO_2Si, M + H]^+$: 427.11, Found 427.12.

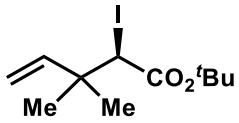


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(chloromethyl)-2-iodopent-4-enoate, 5q: Colorless semi-oil, TLC R_f = 0.80 (Hexane/EtOAc = 30:1, v/v), 66% yield, regioisomers ratio = >95:5, *anti* / *syn* > 95 : 5, 92% ee (ee value was determined by transformation to compound **7q**). $[\alpha]_D^{24}$ +21.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78–5.70 (m, 1H, =CH), 5.30 (d, *J* = 10.5 Hz, 1H, 1/2(=CH_2)), 5.28–5.22 (m, 1H, 1/2(=CH_2)), 4.60 (d, *J* = 7.0 Hz, 1H, CHI), 3.72–3.67 (m, 1H, 1/2(CH_2Cl)), 3.61–3.55 (m, 1H, 1/2(CH_2Cl)), 2.71–2.64 (m, 1H, CH), 1.46 (s, 9H, OC(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (1C, C=O), 136.0 (1C, CH=), 119.5 (1C, =CH_2), 82.7 (1C, O<u>C</u>(CH_3)$_3$), 48.6 (1C, CH_2Cl), 46.5 (1C, CHI), 27.7 (1C, CH), 27.6 (3C, OC(<u>C</u>H_3)$_3$). IR (neat): 2980, 2933, 1726, 1370, 1276, 1156, 928, 844, 748 cm^{-1}. APCI-MS calcd for [$C_{10}H_{17}ClIO_2$, M + H]$^+$: 331.00, Found 331.02.

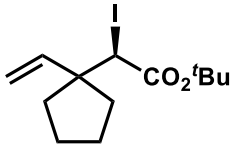


(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(((4-methyl-*N*-phenylphenyl)sulfonamido)methyl)pent-4-enoate, 5r: Colorless semi-oil, TLC R_f = 0.60 (Hexane/EtOAc = 6:1, v/v), 58% yield, regioisomers ratio > 95 : 5, *anti* / *syn* = 95 : 5, 87% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95 : 5, 0.8 mL/min, 210 nm UV detecter, t_R= 21.65 min (minor) and t_R= 27.89 min (major). $[\alpha]_D^{25}$ +8.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.5 Hz, 2H, ArH), 7.32–7.28 (m, 3H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 7.04–6.99 (m, 2H, ArH), 5.70–5.60 (m, 1H, =CH), 5.23 (d, *J* = 10.5 Hz, 1H, 1/2(=CH_2)), 5.08 (d, *J* = 17.0 Hz, 1H, 1/2(=CH_2)), 4.43 (d, *J* = 6.0 Hz, 1H, CHI), 3.80–3.74 (m, 1H, 1/2(CH_2N)), 3.63–3.57 (m, 1H, 1/2(CH_2N)), 2.42 (s, 3H, ArCH_3),

2.40–2.34 (m, 1H, CH), 1.41 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (1C, C=O), 143.5 (1C, ArC), 139.0 (1C, ArC), 136.3 (1C, CH=), 134.7 (1C, ArC), 129.4 (2C, ArC), 129.0 (2C, ArC), 128.8 (2C, ArC), 128.0 (1C, ArC), 127.8 (2C, ArC), 119.4 (1C, $=CH_2$), 82.5 (1C, $O\underline{C}(CH_3)_3$), 52.8 (1C, CH_2N), 45.9 (1C, CHI), 27.9 (1C, CH), 27.6 (3C, $OC(\underline{C}H_3)_3$), 21.5 (1C, $ArCH_3$). IR (neat): 2980, 2931, 1724, 1596, 1493, 1455, 1368, 1350, 1277, 1163, 1092, 917, 815, 727, 696, 657 cm^{-1}. APCI-MS calcd for $[C_{23}H_{29}INO_4S, M + H]^+$: 542.09, Found 542.09.

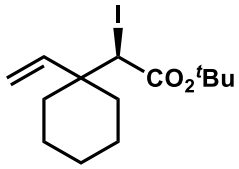


(+)-*tert*-Butyl (*R*)-2-iodo-3,3-dimethylpent-4-enoate, 5s: Colorless semi-oil, TLC R_f = 0.75 (Hexane/EtOAc = 30:1, v/v), 82% yield, regioisomers ratio = >95:5, 91% ee (ee value was determined by transformation to compound **6s**). $[\alpha]_D^{24}$ +5.3 (*c* 0.60, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 5.94 (dd, J_1 = 17.5 Hz and J_2 = 10.5 Hz, 1H, CH=), 5.09 (dd, J_1 = 10.5 Hz and J_2 = 1.0 Hz, 1H, 1/2(=CH_2)), 5.06 (s, 1H, 1/2(=CH_2)), 4.16 (s, 1H, CHI), 1.44 (s, 9H, $C(CH_3)_3$), 1.27 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (1C, C=O), 142.7 (1C, =CH), 113.6 (1C, $=CH_2$), 81.9 (1C, $O\underline{C}(CH_3)_3$), 39.4 (1C, C), 38.9 (1C, CHI), 27.6 (3C, $OC(\underline{C}H_3)_3$), 25.9 (1C, CH_3), 24.9 (1C, CH_3). IR (neat): 2975, 2930, 1732, 1368, 1257, 1167, 1127, 919, 847 cm^{-1}. APCI-MS calcd for $[C_{11}H_{20}IO_2, M + H]^+$: 311.05, Found 311.05.

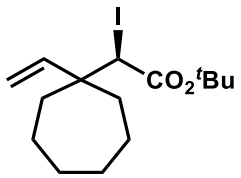


(+)-*tert*-Butyl (*R*)-2-iodo-2-(1-vinylcyclopentyl)acetate, 5t: Colorless semi-oil, TLC R_f = 0.70 (Hexane/EtOAc = 30:1, v/v), 73% yield, regioisomers ratio = >95:5, 92% ee (ee value was determined by transformation to compound **S11t**). $[\alpha]_D^{25}$ +19.2 (*c* 0.50,

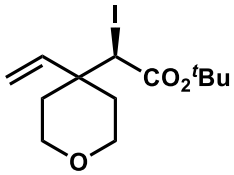
CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 5.95 (dd, J_1 = 17.5 Hz and J_2 = 10.5 Hz, 1H, CH=), 5.16 (d, J = 11.0 Hz, 1H, 1/2(=CH_2)), 5.09 (d, J = 17.5 Hz, 1H, 1/2(=CH_2)), 4.35 (s, 1H, CHI), 1.94–1.87 (m, 1H, 1/2CH_2), 1.81–1.75 (m, 1H, 1/2CH_2), 1.74–1.58 (m, 6H, 3CH_2), 1.43 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (1C, C=O), 140.8 (1C, CH=), 114.5 (1C, =CH_2), 81.8 (1C, O$\underline{C}(CH_3)_3$), 51.5 (1C, C), 38.2 (1C, CHI), 36.2 (1C, CH_2), 36.1 (1C, CH_2), 27.6 (3C, OC($\underline{C}H_3)_3$), 24.1 (1C, CH_2), 24.0 (1C, CH_2). IR (neat): 2959, 1731, 1368, 1161, 1120, 917, 849 cm^{-1}. APCI-MS calcd for [$C_{13}H_{22}IO_2$, M + H]$^+$: 337.07, Found 337.07.



(+)-*tert*-Butyl (*R*)-2-iodo-2-(1-vinylcyclohexyl)acetate, 5u: Colorless semi-oil, TLC R_f = 0.80 (Hexane/EtOAc = 30:1, v/v), 72% yield, regioisomers ratio > 95:5, 85% ee (ee value was determined by transformation to compound **S11u**). $[\alpha]_D^{24}$ +8.0 (*c* 0.30, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 5.74 (dd, J_1 = 17.5 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.31 (dd, J_1 = 11.0 Hz and J_2 = 1.0 Hz, 1H, 1/2(=CH_2)), 5.10 (dd, J_1 = 18.0 Hz and J_2 = 1.0 Hz, 1H, 1/2(=CH_2)), 4.19 (s, 1H, CHI), 1.70–1.40 (m, 10H, 5CH_2), 1.43 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (1C, C=O), 140.0 (1C, =CH), 116.9 (1C, =CH_2), 81.8 (1C, O$\underline{C}(CH_3)_3$), 42.0 (1C, C), 41.0 (1C, CHI), 34.0 (1C, CH_2), 33.7 (1C, CH_2), 27.7 (3C, OC($\underline{C}H_3)_3$), 25.9 (1C, CH_2), 22.5 (1C, CH_2), 22.0 (1C, CH_2). IR (neat): 2933, 2857, 1732, 1455, 1368, 1152, 1118, 921, 847 cm^{-1}. APCI-MS calcd for [$C_{14}H_{24}IO_2$, M + H]$^+$: 351.08, Found 351.10.

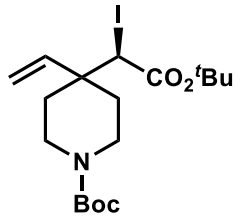


(+)-*tert*-Butyl (*R*)-2-iodo-2-(1-vinylcycloheptyl)acetate, 5v: Colorless semi-oil, TLC R_f = 0.75 (Hexane/EtOAc = 30:1, v/v), 74% yield, regioisomers ratio = >95:5, 91% ee (ee value was determined by transformation to compound **S11v**). $[\alpha]_D^{24}$ +8.8 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (dd, J_1 = 17.5 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.18 (dd, J_1 = 11.0 Hz and J_2 = 0.5 Hz, 1H, 1/2(=CH_2)), 5.04 (d, J = 17.5 Hz, 1H, 1/2(=CH_2)), 4.23 (s, 1H, CHI), 1.91–1.77 (m, 2H, CH_2), 1.75–1.67 (m, 2H, CH_2), 1.67–1.54 (m, 4H, 2CH_2), 1.50–1.45 (m, 4H, 2CH_2), 1.43 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (1C, C=O), 142.8 (1C, CH=), 114.3 (1C, =CH_2), 81.8 (1C, O$\underline{C}(CH_3)_3$), 45.0 (1C, C), 40.5 (1C, CHI), 36.3 (1C, CH_2), 34.7 (1C, CH_2), 29.6 (1C, CH_2), 29.5 (1C, CH_2), 27.6 (3C, OC($\underline{C}H_3)_3$), 23.2 (1C, CH_2), 22.6 (1C, CH_2). IR (neat): 2925, 2857, 1731, 1368, 1117, 915, 849 cm^{-1}. APCI-MS calcd for $[C_{15}H_{26}IO_2, M + H]^+$: 365.10, Found 365.10.



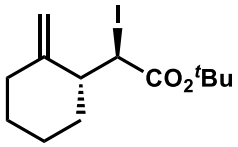
(+)-*tert*-Butyl (*R*)-2-iodo-2-(4-vinyltetrahydro-2H-pyran-4-yl)acetate, 5w: Colorless semi-oil, TLC R_f = 0.35 (Hexane/EtOAc = 10:1, v/v), 75% yield, regioisomers ratio > 95 : 5, 92% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 280 nm UV detecter, t_R= 8.28 min (major) and t_R= 8.84 min (minor). $[\alpha]_D^{25}$ +14.5 (*c* 0.44, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.74 (dd, J_1 = 18.0 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.45 (d, J = 11.0 Hz, 1H, 1/2(=CH_2)), 5.16 (d, J = 17.5 Hz, 1H, 1/2(=CH_2)), 4.14 (s, 1H, CHI), 3.80–3.74 (m, 2H, CH_2O), 3.53 (qd,

J_1 = 12.0 Hz and J_2 = 2.5 Hz, 2H, CH_2O), 2.07–1.96 (m, 2H, CH_2), 1.82–1.74 (m, 1H, 1/2CH_2), 1.55–1.51 (m, 1H, 1/2CH_2), 1.43 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 (1C, C=O), 138.0 (1C, CH=), 118.7 (1C, $=CH_2$), 82.1 (1C, $O\underline{C}(CH_3)_3$), 64.3 (1C, CH_2O), 64.2 (1C, CH_2O), 40.3 (1C, C), 40.1 (1C, CHI), 34.4 (1C, CH_2), 33.9 (2C, $2CH_2$), 27.6 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2976, 2853, 1729, 1368, 1250, 1143, 1109, 1017, 997, 930, 842 cm^{-1}. APCI-MS calcd for [$C_{13}H_{22}IO_3$, M + H]+: 353.06, Found 353.06.



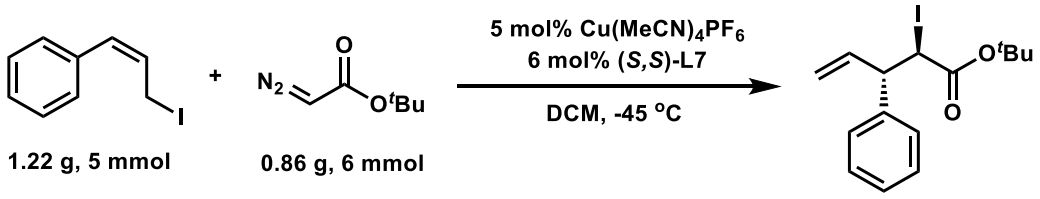
(+)-*tert*-Butyl

(*R*)-4-(2-(*tert*-butoxy)-1-iodo-2-oxoethyl)-4-vinylpiperidine-1-carboxylate, 5x: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 4:1, v/v), 36% yield, regioisomers ratio > 95 : 5, 82% ee. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 210 nm UV detecter, t_R= 10.58 min (major) and t_R= 11.25 min (minor). $[\alpha]_D^{25}$ +24.0 (*c* 0.15, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 5.71 (dd, J_1 = 18.0 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.42 (d, J = 11.0 Hz, 1H, 1/2($=CH_2$)), 5.14 (d, J = 18.0 Hz, 1H, 1/2($=CH_2$)), 4.12 (s, 1H, CHI), 3.97–3.72 (m, 2H, NCH_2), 2.87 (brs, 2H, NCH_2), 2.08–2.00 (m, 1H, 1/2CH_2), 1.84 (td, J_1 = 13.0 Hz and J_2 = 4.5 Hz, 1H, 1/2CH_2), 1.63–1.53 (m, 2H, CH_2), 1.43 (s, 9H, $C(CH_3)_3$), 1.41 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 (1C, C=O), 154.7 (1C, C=O), 137.7 (1C, CH=), 118.7 (1C, $=CH_2$), 82.2 (1C, $O\underline{C}(CH_3)_3$), 79.5 (1C, $O\underline{C}(CH_3)_3$), 41.0 (1C, CHI), 39.5 (1C, C), 33.5 (2C, $2NCH_2$), 32.9 (2C, $2CH_2$), 28.4 (3C, $OC(\underline{C}H_3)_3$), 27.6 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2977, 2934, 1729, 1694, 1423, 1367, 1279, 1248, 1162, 999, 926, 849, 770 cm^{-1}. APCI-MS calcd for [$C_{18}H_{31}INO_4$, M + H]+: 452.13, Found 452.13.

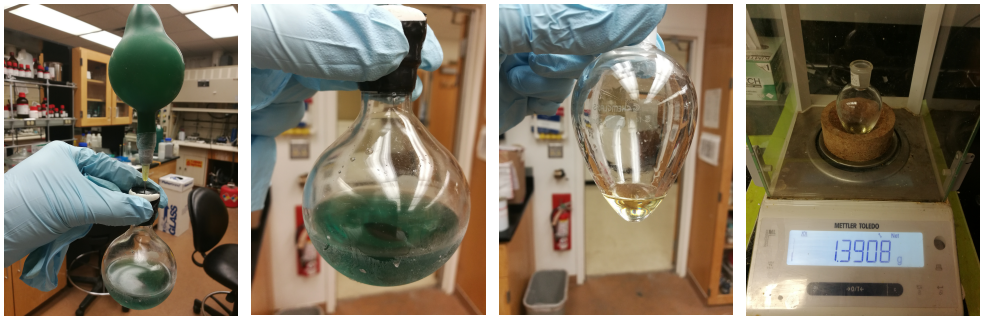


(+)-*tert*-Butyl (*R*)-2-iodo-2-((*R*)-2-methylenecyclohexyl)acetate, 5y: Colorless semi-oil, TLC R_f = 0.70 (Hexane/EtOAc = 30:1, v/v), 82% yield, regioisomers ratio > 95 : 5, *anti* / *syn* = >95 : 5, 93% ee (ee value was determined by transformation to compound **6y**). $[\alpha]_D^{24}$ +25.6 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.85 (s, 1H, 1/2(=CH_2)), 4.71 (s, 1H, 1/2(=CH_2)), 4.43 (d, *J* = 11.5 Hz, 1H, CHI), 2.80–2.72 (m, 1H, CH), 2.16–2.01 (m, 2H, CH_2), 1.79–1.50 (m, 6H, 3CH_2), 1.47 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (1C, C=O), 148.5 (1C, =C), 110.3 (1C, =CH_2), 81.9 (1C, O<u>C</u>$(CH_3)_3$), 47.6 (1C, CHI), 32.8 (1C, CH), 30.4 (1C, CH_2), 28.4 (1C, CH_2), 28.1 (1C, CH_2), 27.6 (3C, OC(<u>C</u>$H_3)_3$), 22.3 (1C, CH_2). IR (neat): 2979, 2933, 2859, 1731, 1451, 1369, 1282, 1152, 1132, 893, 844 cm^{-1}. APCI-MS calcd for $[C_{13}H_{22}IO_2, M + H]^+$: 337.07, Found 337.09.

6. Gram-Scale Experiment



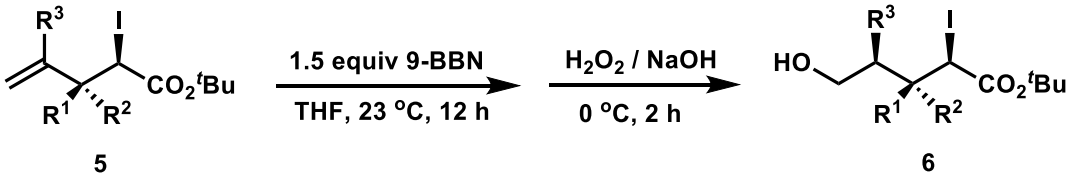
1.39 g
77% yield, >95:5 rr
>95:5 dr, 97% ee



A 100 mL flask was charged with $[Cu(MeCN)_4]PF_6$ (93.0 mg, 0.25 mmol) and (*S*,*S*)-L7 (88.2 mg, 0.3 mmol). The flask was then evacuated and refilled with Argon. After dry CH_2Cl_2 (30 mL) was added, the mixture was stirred at 23 °C for 2 h. Then the mixture was cooled to –45 °C, followed by addition of a mixed solution of (*Z*)-**1a** (1.22 g, 5 mmol) and **2b** (0.86 g, 6 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at –45 °C until the reaction was complete (48 h), and then the mixture was concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 30:1) to afford 1.39 g desired [2,3]-rearrangement products **5a** as a light yellow oil, 77% yield, >95:5 r.r., 95:5 d.r., and 97% ee.

7. Transformations of [2,3]-Rearrangement Products

7A. Conversion of terminal C=C double bond to alcohol

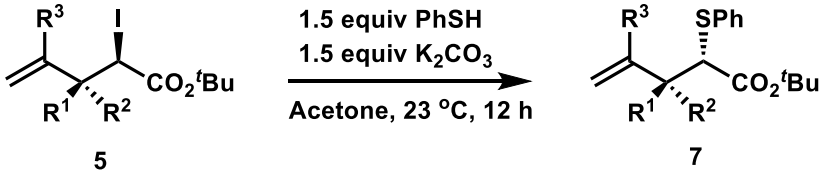


5 6

Typical procedure: An 8 mL reaction vial was charged with [2,3]-rearrangement product (**5**, 0.1 mmol) and dry THF (2 mL). The mixture was stirred at 0 °C, followed by addition of 9-BBN (0.5 M in THF, 0.3 mL, 0.15 mmol). The mixture was then warmed to 23 °C and stirred for 12 h. The reaction was cooled to 0 °C again and treated with H_2O

(0.2 mL) and a mixed solution of aqueous NaOH (3N, 0.1 mL) and H_2O_2 (30%, 0.2 mL). Two hours later, the reaction solution was diluted with H_2O (5 mL) and Et_2O (25 mL). The organic layer was separated, washed with H_2O (5 mL x 2), concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) to afford alcohol product **6**.

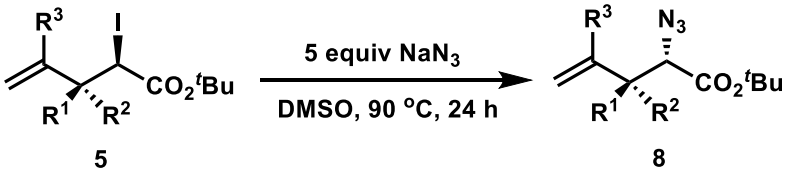
7B. Transformation of C–I bond to C–S bond



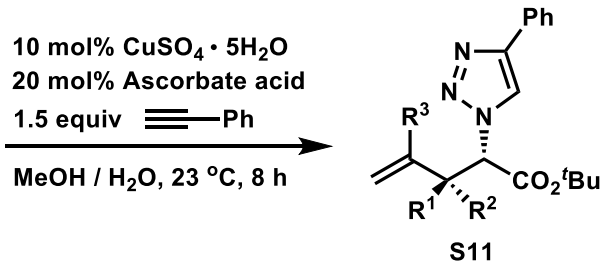
5 7

Typical procedure: An 8 mL reaction vial was charged with PhSH (17 mg, 0.15 mmol), K_2CO_3 (21 mg, 0.15 mmol) and acetone (2 mL). The mixture was stirred at 23 °C for 10 min and then treated with a solution of [2,3]-rearrangement product (**5**, 0.1 mmol), acetone (1 mL). The reaction was stirred at 23 °C for 12 h, concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 30:1) to afford desired product **7**.

7C. Transformation of C–I bond to C–N bond



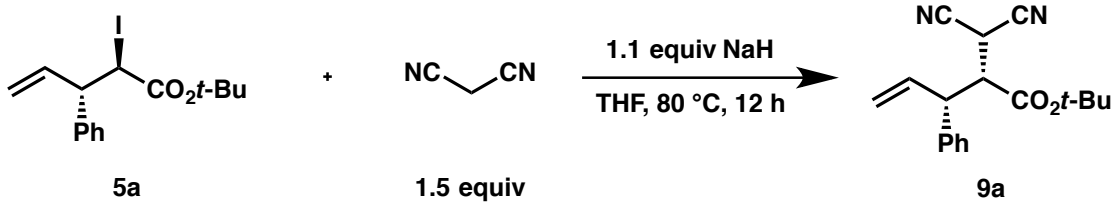
5 8



S11

Typical procedure: An 8 mL reaction vial was charged with NaN_3 (65 mg, 1 mmol), [2,3]-rearrangement product (**5**, 0.2 mmol) and dry DMSO (2 mL). The mixture was stirred at 90 ^oC for 24 hours, then cooled to 23 ^oC and diluted with H_2O (5 mL) and Et_2O (40 mL). The organic layer was separated, washed with H_2O (5 mL x 2), concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 30:1) to afford alcohol product **8**. An 8 mL reaction vial was charged with $CuSO_4{\cdot}5H_2O$ (2.5 mg, 0.01 mmol), Ascorbate acid (CAS NO. 134-03-2, 4.2 mg, 0.02 mmol), H_2O (1 mL) and MeOH (1 mL). The mixture was stirred at room temperature for 5 min, followed by addition of phenylacetylene (16 mg, 0.15 mmol). After 2 additional min, a solution of [2,3]-rearrangement product (**5**, 0.1 mmol) in MeOH (1 mL) was added. The mixture was stirred at 23 ^oC for 12 h. The mixture was then extracted by CH_2Cl_2 (10 mL x 3). The organic layer was combined, concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 8:1) to afford cycloaddition product **S11**.

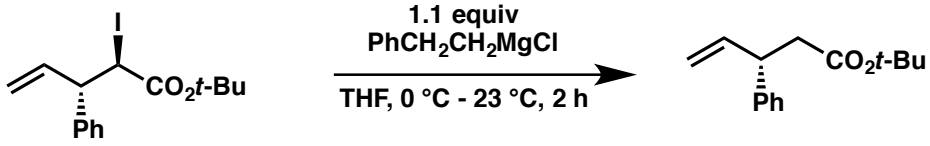
7D. Transformation of C–I bond to C–C bond



Typical procedure: An 8 mL reaction vial was charged with NaH (60wt%, 4.5 mg, 0.11 mmol), malononitrile (10 mg, 0.15 mmol) and dry THF (1 mL). The mixture was stirred at 23 ^oC for 30 minutes and then treated with a solution of [2,3]-rearrangement product (**5a**, 0.1 mmol) in THF (1mL). The reaction was then stirred at 80 ^oC in an oil bath for 12 h, quenched with H_2O (10 μL), concentrated and diluted in Et_2O (15 mL) and EtOAc (15 mL). The organic layer was washed with H_2O (10 mL x 3), concentrated and purified by

flash column chromatography on silica gel (Hexane/EtOAc = 10:1) to afford desired product **9a**.

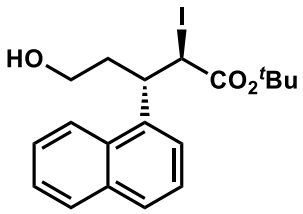
7E. Transformation of C–I bond to C–H bond



5a **10a**

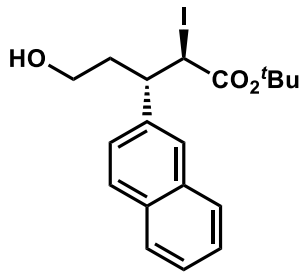
Typical procedure: An 8 mL reaction vial was charged with [2,3]-rearrangement product (**5a**, 0.1 mmol) and dry THF (1 mL). The mixture was stirred at 0 ^{o}C and treated with $PhCH_2CH_2MgCl$ (1.0 M in THF, 110 μL, 0.11 mmol). Two hours later, 10 μL H_2O was added and the reaction solution was concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 30:1) to afford desired product **10a**.

8. Characterization Data for Transformation Products



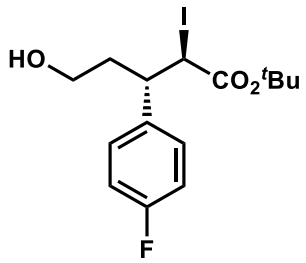
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(naphthalen-1-yl)pentanoate, 6c: Colorless semi-oil, TLC R_f = 0.35 (Hexane/EtOAc = 5:1, v/v), 88% yield, *anti* / *syn* > 95 : 5, 90% ee. HPLC conditions: Chiralcel OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 85:15, 0.8 mL/min, 220 nm UV detecter, t_R= 9.02 min (minor) and t_R= 18.91 min (major). $[\alpha]_D^{24}$ +12.0 (*c* 0.30, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.5 Hz, 1H, ArH), 7.83 (d, *J* = 8.0 Hz, 1H, ArH), 7.74 (d, *J* = 8.0 Hz, 1H, ArH), 7.55 (t, *J* = 7.5 Hz, 1H, ArH), 7.49 (t, *J* = 7.5 Hz, 1H, ArH), 7.45 (t, *J* = 7.5 Hz, 1H,

ArH), 7.38 (d, J = 7.0 Hz, 1H, ArH), 4.68 (d, J = 11.0 Hz, 1H, CHI), 4.25 (td, J_1 = 11.0 Hz and J_2 = 3.0 Hz, 1H, ArCH), 3.54–3.47 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.37–3.29 (m, 1H, 1/2(HOC$\underline{H}_2$)), 2.68–2.59 (m, 1H, 1/2CH_2), 1.97–1.88 (m, 1H, 1/2CH_2), 1.22 (brs, 1H, OH), 0.87 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, $\underline{C}O_2C(CH_3)_3$), 136.7 (1C, ArC), 133.8 (1C, ArC), 132.3 (1C, ArC), 128.8 (1C, ArC), 127.8 (1C, ArC), 126.3 (1C, ArC), 125.8 (1C, ArC), 125.3 (1C, ArC), 123.6 (1C, ArC), 123.5 (1C, ArC), 81.6 (1C, O$\underline{C}(CH_3)_3$), 60.2 (1C, $HOCH_2$), 40.0 (1C, ArCH), 39.1 (1C, CH_2), 32.0 (1C, CHI), 26.9 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2929, 1720, 1368, 1284, 1156, 843, 781 cm^{-1}. APCI-MS calcd for $[C_{19}H_{24}IO_3, M + H]^+$: 427.08, Found 427.08.

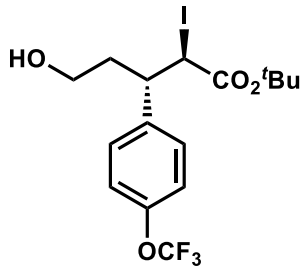


(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(naphthalen-2-yl)pentanoate, 6d: Colorless semi-oil, TLC R_f = 0.35 (Hexane/EtOAc = 5:1, v/v), 84% yield, *anti* / *syn* = 93 : 7, 96% ee. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 85:15, 0.5 mL/min, 210 nm UV detecter, t_R= 11.67 min (major) and t_R= 14.27 min (minor). $[\alpha]_D^{23}$ +3.5 (*c* 0.80, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.75 (m, 3H, ArH), 7.65 (s, 1H, ArH), 7.49–7.43 (m, 2H, ArH), 7.31 (dd, J_1 = 8.5 Hz and J_2 = 1.5 Hz, 1H, ArH), 4.55 (d, J = 11.5 Hz, 1H, CHI), 3.56–3.50 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.44 (td, J_1 = 11.5 Hz and J_2 = 3.0 Hz, 1H, ArCH), 3.41–3.35 (m, 1H, 1/2(HOC$\underline{H}_2$)), 2.58–2.49 (m, 1H, 1/2CH_2), 1.93–1.84 (m, 1H, 1/2CH_2), 1.74–1.63 (m, 1H, OH), 1.08 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (1C, $\underline{C}O_2C(CH_3)_3$), 136.5 (1C, ArC), 133.2 (1C, ArC), 132.7 (1C, ArC), 128.4 (1C, ArC), 127.7 (1C, ArC), 127.6 (1C, ArC), 127.4 (1C, ArC), 126.2 (1C, ArC), 125.9 (1C, ArC), 125.6 (1C, ArC), 81.8 (1C, O$\underline{C}(CH_3)_3$), 60.4 (1C, $HOCH_2$), 46.7 (1C, ArCH), 38.4 (1C, CH_2), 31.1 (1C,

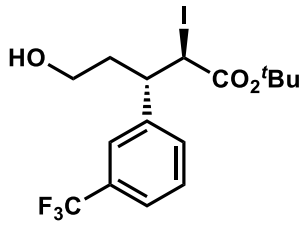
CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2976, 2929, 1725, 1368, 1282, 1155, 1049, 819, 746 cm^{-1}. APCI-MS calcd for $[C_{19}H_{24}IO_3, M + H]^+$: 427.08, Found 427.08.



(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-fluorophenyl)-5-hydroxy-2-iodopentanoate, 6h: Colorless semi-oil, TLC R_f = 0.30 (Hexane/EtOAc = 5:1, v/v), 80% yield, *anti* / *syn* = 92 : 8, 93% ee, HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detecter, t_R= 10.18 min (major) and t_R= 12.24 min (minor). $[\alpha]_D^{23}$ +2.0 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19–7.13 (m, 2H, ArH), 7.05–6.95 (m, 2H, ArH), 4.38 (d, *J* = 11.0 Hz, 1H, CHI), 3.56–3.49 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.38–3.31 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.26 (td, J_1 = 11.5 Hz and J_2 = 3.0 Hz, 1H, ArCH), 2.51–2.43 (m, 1H, 1/2CH_2), 1.76–1.68 (m, 1H, 1/2CH_2), 1.63 (brs, 1H, OH), 1.19 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (1C, $\underline{C}O_2C(CH_3)_3$), 161.9 (d, *J* = 245.2 Hz, 1C, ArC), 134.8 (d, *J* = 3.3 Hz, 1C, ArC), 129.7 (d, *J* = 8.0 Hz, 2C, ArC), 115.5 (d, *J* = 21.3 Hz, 2C, ArC), 81.9 (1C, O$\underline{C}(CH_3)_3$), 60.2 (1C, $HOCH_2$), 45.9 (1C, ArCH), 38.4 (1C, CH_2), 30.8 (1C, d, *J* = 1.2 Hz, CHI), 27.3 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2977, 2932, 1724, 1602, 1508, 1368, 1226, 1159, 1049, 837, 728 cm^{-1}. APCI-MS calcd for $[C_{15}H_{21}FIO_3, M + H]^+$: 395.05, Found 395.05.

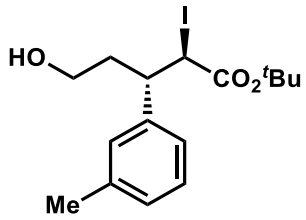


(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(4-(trifluoromethoxy)phenyl)pentanoate, 6i: White solid, mp: 89–90 °C. TLC R_f = 0.50 (Hexane/EtOAc = 5:1, v/v), 75% yield, *anti* / *syn* > 95 : 5, 93% ee, HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.8 mL/min, 220 nm UV detecter, t_R= 9.30 min (major) and t_R= 10.88 min (minor). $[\alpha]_D^{25}$ +2.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.21 (m, 12H, ArH), 7.18–7.12 (m, 2H, ArH), 4.39 (d, *J* = 11.0 Hz, 1H, CHI), 3.59–3.51 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.40–3.34 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.31 (td, J_1 = 11.5 Hz and J_2 = 3.0 Hz, 1H, ArCH), 2.53–2.44 (m, 1H, 1/2CH_2), 1.78–1.70 (m, 1H, 1/2CH_2), 1.25 (brs, 1H, OH), 1.16 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (1C, $\underline{C}O_2C(CH_3)_3$), 148.3 (q, *J* = 1.7 Hz, 1C, ArC), 138.0 (1C, ArC), 129.5 (2C, ArC), 121.2 (2C, ArC), 120.4 (q, *J* = 256 Hz, 1C, CF_3), 82.0 (1C, O$\underline{C}(CH_3)_3$), 60.1 (1C, $HOCH_2$), 46.1 (1C, ArCH), 38.3 (1C, CH_2), 30.3 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2927, 1720, 1506, 1372, 1271, 1213, 1163, 1129, 1047, 841 cm^{-1}. APCI-MS calcd for $[C_{16}H_{21}F_3IO_4, M + H]^+$: 461.04, Found 461.04.



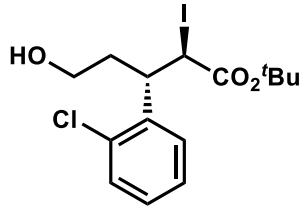
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(3-(trifluoromethyl)phenyl)pentanoate, 6j: Colorless semi-oil, TLC R_f = 0.30 (Hexane/EtOAc = 5:1, v/v), 76% yield, *anti* / *syn* = 95 : 5, 97% ee, HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detecter, t_R= 6.71 min (major) and

t_R= 7.42 min (minor). $[\alpha]_D^{25}$ +4.0 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.49 (m, 1H, ArH), 7.48–7.38 (m, 3H, ArH), 4.44 (d, *J* = 11.2 Hz, 1H, CHI), 3.60–3.51 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.42–3.30 (m, 2H, 1/2(HOC$\underline{H}_2$)+ ArCH), 2.56–2.44 (m, 1H, 1/2CH_2), 1.84–1.74 (m, 1H, 1/2CH_2), 1.26–1.20 (brs, 1H, OH), 1.16 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, $\underline{C}O_2C(CH_3)_3$), 140.4 (1C, ArC), 131.4 (1C, ArC), 130.9 (q, *J* = 32.1 Hz, 1C, ArC), 129.1 (1C, ArC), 125.0 (q, *J* = 3.8 Hz, 1C, ArC), 124.3 (q, *J* = 3.8 Hz, 1C, ArC), 123.9 (q, *J* = 271 Hz, 1C, CF_3), 82.1 (1C, O$\underline{C}(CH_3)_3$), 60.0 (1C, $HOCH_2$), 46.5 (1C, ArCH), 38.2 (1C, CH_2), 30.0 (1C, CHI), 27.1 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2980, 2934, 1726, 1328, 1164, 1128, 1076, 843, 806, 704 cm^{-1}. APCI-MS calcd for $[C_{16}H_{21}F_3IO_3, M + H]^+$: 445.05, Found 445.05.

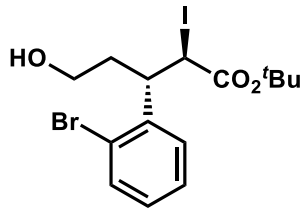


(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(*m*-tolyl)pentanoate, 6k: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 5:1, v/v), 86% yield, *anti* / *syn* > 95 : 5, 94% ee, HPLC conditions: Chiralcel OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 230 nm UV detecter, t_R= 7.27 min (minor) and t_R= 8.96 min (major). $[\alpha]_D^{25}$ +1.5 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.5 Hz, 1H, ArH), 7.04 (d, *J* = 7.5 Hz, 1H, ArH), 7.00–6.95 (m, 2H, ArH), 4.41 (d, *J* = 11.0 Hz, 1H, CHI), 3.56–3.49 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.43–3.36 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.20 (td, J_1 = 11.5 Hz and J_2 = 3.0 Hz, 1H, ArCH), 2.50–2.41 (m, 1H, 1/2CH_2), 2.31 (s, 3H, CH_3), 1.81–1.72 (m, 1H, 1/2CH_2), 1.23 (brs, 1H, OH), 1.17 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (1C, $\underline{C}O_2C(CH_3)_3$), 138.9 (1C, ArC), 138.1 (1C, ArC), 128.9 (1C, ArC), 128.5 (1C, ArC), 128.2 (1C, ArC), 125.0 (1C, ArC), 81.6 (1C, O$\underline{C}(CH_3)_3$), 60.6 (1C, $HOCH_2$), 46.8 (1C, ArCH), 38.5 (1C, CH_2), 31.4 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$), 21.4 (1C, CH_3). IR

(neat): 2977, 2930, 1727, 1368, 1257, 1155, 1050, 844, 705 cm^{-1}. APCI-MS calcd for $[C_{16}H_{24}IO_3, M + H]^+$: 391.08, Found 391.08.

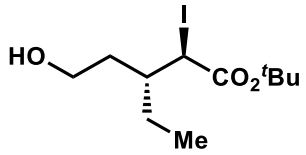


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-chlorophenyl)-5-hydroxy-2-iodopentanoate, 6l: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 5:1, v/v), 76% yield, *anti* / *syn* > 95 : 5, 95% ee, HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 210 nm UV detecter, t_R= 11.02 min (major) and t_R= 12.37 min (minor). $[\alpha]_D^{25}$ +6.1 (*c* 0.33, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.25–7.15 (m, 3H, ArH), 4.75–4.35 (m, 1H, CHI), 3.97–3.62 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.58–3.42 (m, 2H, 1/2(HOC$\underline{H}_2$)+ArCH), 2.52–2.40 (m, 1H, 1/2CH_2), 1.95–1.65 (m, 1H, 1/2CH_2), 1.49–1.37 (m, 1H, OH), 1.19 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, C=O), 137.6 (1C, ArC), 134.4 (1C, ArC), 129.9 (1C, ArC), 128.5 (2C, ArC), 127.2 (1C, ArC), 82.0 (1C, O$\underline{C}(CH_3)_3$), 60.1 (1C, $HOCH_2$), 42.0 (1C, ArCH), 38.3 (1C, CH_2), 30.1 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2929, 1725, 1475, 1368, 1288, 1258, 1157, 1051, 754 cm^{-1}. APCI-MS calcd for $[C_{15}H_{21}ClIO_3, M + H]^+$: 411.02, Found 411.02.

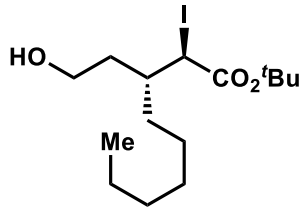


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-bromophenyl)-5-hydroxy-2-iodopentanoate, 6m: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 5:1, v/v), 72% yield, *anti* / *syn* > 95 :

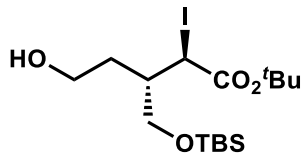
5, 95% ee, HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 210 nm UV detecter, t_R= 11.49 min (major) and t_R= 13.38 min (minor). $[\alpha]_D^{24}$ +4.8 (*c* 0.33, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H, ArH), 7.30 (t, *J* = 7.5 Hz, 1H, ArH), 7.21 (dd, J_1 = 8.0 Hz and J_2 = 1.0 Hz, 1H, ArH), 7.09 (td, J_1 = 8.0 Hz and J_2 = 2.0 Hz, 1H, ArH), 4.54 (d, *J* = 10.5 Hz, 1H, CHI), 3.90–3.73 (m, 1H, 1/2(HOC$\underline{H}_2$)), 3.59–3.41 (m, 2H, 1/2(HOC$\underline{H}_2$)+ArCH), 2.54–2.36 (m, 1H, 1/2CH_2), 1.86–1.72 (m, 1H, 1/2CH_2), 1.52 (brs, 1H, OH), 1.20 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (1C, C=O), 139.4 (1C, ArC), 133.1 (1C, ArC), 128.7 (1C, ArC), 127.8 (1C, ArC), 127.4 (1C, ArC), 125.5 (1C, ArC), 82.1 (1C, O$\underline{C}(CH_3)_3$), 59.9 (1C, $HOCH_2$), 44.8 (1C, ArCH), 38.6 (1C, CH_2), 30.4 (1C, CHI), 27.2 (3C, OC($\underline{C}H_3)_3$). IR (neat): 2925, 1723, 1472, 1368, 1257, 1157, 1051, 754, 668 cm^{-1}. APCI-MS calcd for $[C_{15}H_{21}BrIO_3, M + H]^+$: 454.97, Found 454.97.



(+)-*tert*-Butyl (2*R*, 3*R*)-3-ethyl-5-hydroxy-2-iodopentanoate, 6n: Colorless semi-oil, TLC R_f = 0.45 (Hexane/EtOAc = 5:1, v/v), 84% yield, *anti* / *syn* > 95 : 5, 93% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.5 mL/min, 280 nm UV detecter, t_R= 10.38 min (major) and t_R= 11.76 min (minor). $[\alpha]_D^{24}$ +18.0 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.42 (d, *J* = 6.0 Hz, 1H, CHI), 3.75–3.61 (m, 2H, OCH_2), 1.95–1.87 (m, 1H, CH), 1.78 (brs, 1H, OH), 1.60–1.48 (m, 3H, CH_2+1/2CH_2), 1.46 (s, 9H, $C(CH_3)_3$), 1.41–1.32 (m, 1H, 1/2CH_2), 0.91 (t, *J* = 7.5 Hz, 1H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (1C, C=O), 82.3 (1C, O$\underline{C}(CH_3)_3$), 60.4 (1C, $HOCH_2$), 39.2 (1C, CHI), 36.7 (1C, CH), 33.3 (1C, CH_2), 27.6 (3C, OC($\underline{C}H_3)_3$), 25.3 (1C, CH_2), 11.1 (1C, CH_3). IR (neat): 2931, 1727, 1368, 1156, 1055, 845 cm^{-1}. APCI-MS calcd for $[C_{11}H_{22}IO_3, M + H]^+$: 329.06, Found 329.06.

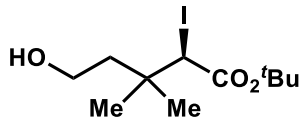


(+)-*tert*-Butyl (2*R*, 3*R*)-3-(2-hydroxyethyl)-2-iodononanoate, 6o: Colorless semi-oil, TLC R_f = 0.50 (Hexane/EtOAc = 5:1, v/v), 80% yield, *anti* / *syn* > 95 : 5, 91% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.5 mL/min, 210 nm UV detecter, t_R= 8.56 min (major) and t_R= 9.24 min (minor). $[\alpha]_D^{24}$ +28.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.41 (d, *J* = 6.0 Hz, 1H, CHI), 3.76–3.61 (m, OCH_2), 1.94–1.86 (m, 1H, CH), 1.75 (brs, 1H, OH), 1.65–1.50 (m, 2H, CH_2), 1.46 (s, 9H, $C(CH_3)_3$), 1.37–1.18 (m, 10H, $5CH_2$), 0.87 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0 (1C, C=O), 82.3 (1C, $O\underline{C}(CH_3)_3$), 60.3 (1C, $HOCH_2$), 37.8 (1C, CHI), 37.1 (1C, CH), 33.8 (1C, CH_2), 32.6 (1C, CH_2), 31.7 (1C, CH_2), 29.3 (1C, CH_2), 27.6 (3C, $OC(\underline{C}H_3)_3$), 26.6 (1C, CH_2), 22.6 (1C, CH_2), 14.0 (1C, CH_3). IR (neat): 2928, 2856, 1728, 1368, 1257, 1156, 1122, 845 cm^{-1}. APCI-MS calcd for $[C_{15}H_{30}IO_3, M + H]^+$: 385.12, Found 385.12.

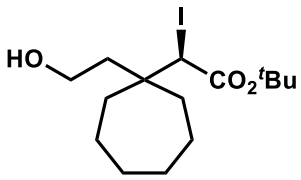


(+)-*tert*-Butyl (2*R*, 3*S*)-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-hydroxy-2-iodopentanoate, 6p: Colorless semi-oil, TLC R_f = 0.55 (Hexane/EtOAc = 5:1, v/v), 78% yield, *anti* / *syn* > 95 : 5, 92% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 97 : 3, 0.4 mL/min, 280 nm UV detecter, t_R= 11.88 min (major) and t_R= 12.32 min (minor). $[\alpha]_D^{25}$ +22.9 (*c* 0.36, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 (d, *J* = 6.0 Hz, 1H, CHI), 3.72–3.64 (m, 3H, $1/2C\underline{H}_2OTBS + C\underline{H}_2OH$), 3.56–3.50 (m,

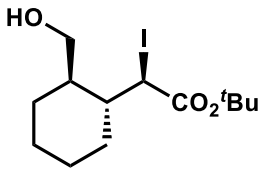
1H, 1/2C$\underline{H}_2$OTBS), 2.54–2.44 (m, 1H, CH), 1.96–1.87 (m, 1H, 1/2CH_2), 1.86–1.80 (m, 1H, OH), 1.59–1.52 (m, 1H, 1/2CH_2), 1.46 (s, 9H, OC$(CH_3)_3$), 0.90 (s, 9H, SiC$(CH_3)_3$), 0.08 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (1C, C=O), 82.3 (1C, O$\underline{C}(CH_3)_3$), 63.9 (1C, $\underline{C}H_2$OTBS), 60.5 (1C, CH_2OH), 41.2 (1C, CHI), 35.3 (1C, CH_2), 29.9 (1C, CH), 27.6 (3C, OC($\underline{C}H_3)_3$), 25.8 (3C, SiC($\underline{C}H_3)_3$), 18.2 (1C, Si$\underline{C}(CH_3)_3$), -5.4 (1C, $SiCH_3$), -5.5 (1C, $SiCH_3$). IR (neat): 2954, 2930, 1727, 1472, 1369, 1256, 1155, 1110, 836, 777 cm^{-1}. APCI-MS calcd for $[C_{16}H_{34}IO_4Si, M + H]^+$: 445.13, Found 445.13.



(+)-*tert*-Butyl (*R*)-5-hydroxy-2-iodo-3,3-dimethylpentanoate, 6s: Colorless semi-oil, TLC R_f = 0.45 (Hexane/EtOAc = 5:1, v/v), 84% yield, 91% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 280 nm UV detecter, t_R= 7.19 min (minor) and t_R= 7.79 min (major). $[\alpha]_D^{24}$ +5.2 (*c* 0.70, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.26 (s, 1H, CHI), 3.73 (t, *J* = 9.0 Hz, 2H, OCH_2), 1.84–1.70 (m, 2H, CH_2), 1.55–1.49 (m, 1H, OH), 1.45 (s, 9H, C$(CH_3)_3$), 1.18 (s, 3H, CH_3), 1.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5 (1C, $\underline{C}O_2C(CH_3)_3$), 82.0 (1C, O$\underline{C}(CH_3)_3$), 59.6 (1C, $HOCH_2$), 42.1 (1C, CHI), 40.6 (1C, CH_2), 35.8 (1C, C), 27.6 (3C, OC($\underline{C}H_3)_3$), 26.3 (1C, CH_3), 24.5 (1C, CH_3). IR (neat): 2971, 2932, 1731, 1369, 1254, 1159, 1129, 847 cm^{-1}. APCI-MS calcd for $[C_{11}H_{22}IO_3, M + H]^+$: 329.06, Found 329.06.

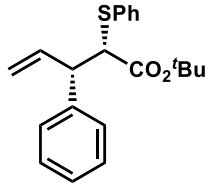


(+)-*tert*-Butyl (*R*)-2-(1-(2-hydroxyethyl)cycloheptyl)-2-iodoacetate, 6v: Colorless semi-oil, TLC R_f = 0.55 (Hexane/EtOAc = 5:1, v/v), 56% yield, 91% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.4 mL/min, 280 nm UV detecter, t_R= 24.36 min (minor) and t_R= 25.32 min (major). $[\alpha]_D^{24}$ +2.4 (*c* 0.33, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.42 (s, 1H, CHI), 3.80–3.70 (m, 2H, OCH_2), 2.02–1.78 (m, 3H, $\underline{H}OCH_2C\underline{H}_2$), 1.72–1.54 (m, 8H, $4CH_2$), 1.50–1.44 (m, 13H, $2CH_2$ + $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7 (1C, $\underline{C}O_2C(CH_3)_3$), 82.0 (1C, $O\underline{C}(CH_3)_3$), 59.3(1C, $HOCH_2$), 42.0 (1C, CHI), 41.2 (1C, C), 40.8 (1C, CH_2), 37.0 (1C, CH_2), 35.5 (1C, CH_2), 30.2 (1C, CH_2), 30.1 (1C, CH_2), 27.6 (3C, $OC(\underline{C}H_3)_3$), 23.7 (1C, CH_2), 23.5 (1C, CH_2). IR (neat): 2923, 2855, 1730, 1459, 1368, 1160, 1122, 1038, 847 cm^{-1}. APCI-MS calcd for $[C_{19}H_{24}IO_3, M + H]^+$: 383.11, Found 383.11.

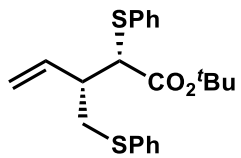


(+)-*tert*-Butyl (2*R*)-2-((1*R*)-2-(hydroxymethyl)cyclohexyl)-2-iodoacetate, 6y: Colorless semi-oil, TLC R_f = 0.45 (Hexane/EtOAc = 5:1, v/v), 70% yield, 93% ee. HPLC conditions: Chiralcel AS-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.5 mL/min, 280 nm UV detecter, t_R= 11.05 min (major) and t_R= 13.20 min (minor). $[\alpha]_D^{24}$ +66.0 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11 (d, *J* = 12.0 Hz, 1H, CHI), 3.68–3.58 (m, 2H, OCH_2), 2.24 (brs, 1H, OH), 2.08–1.98 (m, 2H, 2CH), 1.78–1.64 (m, 2H, CH_2), 1.46 (s, 9H, $C(CH_3)_3$), 1.46–1.12 (m, 6H, $3CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 (1C, $\underline{C}O_2C(CH_3)_3$), 81.9 (1C, $O\underline{C}(CH_3)_3$), 60.2 (1C, $HOCH_2$), 43.0 (1C,

CH), 39.7 (1C, CH), 32.1 (1C, CHI), 28.0 (1C, CH_2), 27.6 (3C, $OC(\underline{C}H_3)_3$), 26.1 (1C, CH_2), 25.4 (1C, CH_2), 20.3 (1C, CH_2). IR (neat): 2929, 2856, 1727, 1368, 1252, 1159, 1130, 1033, 949, 848 cm^{-1}. APCI-MS calcd for $[C_{13}H_{24}IO_3, M + H]^+$: 355.08, Found 355.08.

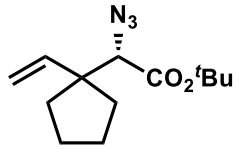


(–)-*tert*-Butyl (2*S*, 3*S*)-3-phenyl-2-(phenylthio)pent-4-enoate, 7a: Colorless semi-oil, TLC R_f = 0.45 (Hexane/EtOAc = 30:1, v/v), 95% yield, *syn* / *anti* > 95 : 5, 97% ee. HPLC conditions: Chiralcel OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.5 mL/min, 210 nm UV detecter, t_R= 8.05 min (minor) and t_R= 8.79 min (major). $[\alpha]_D^{24}$ –18.2 (*c* 0.76, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35–7.20 (m, 10H, ArH), 6.08–5.98 (m, 1H, =CH), 5.17–5.07 (m, 2H, $=CH_2$), 3.94 (d, *J* = 11.0 Hz, 1H, CHS), 3.77–3.71 (m, 1H, CH), 1.33 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3 (1C, C=O), 140.0 (1C, ArC), 138.0 (1C, =CH), 133.8 (1C, ArC), 133.0 (2C, ArC), 128.6 (2C, ArC), 128.5 (2C, ArC), 128.3 (2C, ArC), 127.6 (1C, ArC), 127.1 (1C, ArC), 116.9 (1C, $=CH_2$), 81.6 (1C, $O\underline{C}(CH_3)_3$), 56.7 (1C, CHS), 52.0 (1C, CH), 27.8 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2978, 2931, 1727, 1480, 1368, 1280, 1142, 921, 747, 699 cm^{-1}. APCI-MS calcd for $[C_{21}H_{25}O_2S, M + H]^+$: 341.16, Found 341.16.

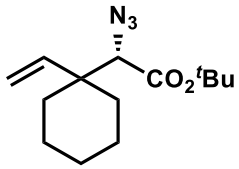


(–)-*tert*-Butyl (2*S*, 3*S*)-2-(phenylthio)-3-((phenylthio)methyl)pent-4-enoate, 7q: Colorless semi-oil, TLC R_f = 0.40 (Hexane/EtOAc = 30:1, v/v), 94% yield, *syn* / *anti* = 94 : 6, 92% ee. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID),

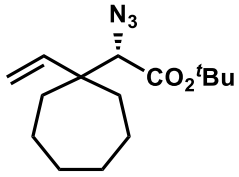
hexane/2-propanol = 95:5, 0.5 mL/min, 210 nm UV detecter, t_R= 10.19 min (major) and t_R= 10.90 min (minor). $[\alpha]_D^{24}$ –31.0 (*c* 0.60, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.42 (m, 2H, ArH), 7.35–7.30 (m, 2H, ArH), 7.29–7.25 (m, 5H, ArH), 7.20–7.16 (m, 1H, ArH), 5.84–5.74 (m, 1H, =CH), 5.22–5.14 (m, 2H, =CH_2), 3.78 (d, J = 8.5 Hz, 1H, CHS), 3.49 (dd, J_1 = 13.0 Hz and J_2 = 4.5 Hz, 1H, 1/2(CH_2S)), 3.05 (dd, J_1 = 13.0 Hz and J_2 = 3.5 Hz, 1H, 1/2(CH_2S)), 2.82–2.74 (m, 1H, CH), 1.34 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8 (1C, C=O), 136.1 (1C, =CH), 133.8 (1C, ArC), 132.5 (2C, ArC), 129.8 (1C, ArC), 129.5 (2C, ArC), 128.9 (4C, ArC), 127.7 (1C, ArC), 126.1 (1C, ArC), 119.0 (1C, =CH_2), 81.8 (1C, O<u>C</u>(CH_3)$_3$), 55.3 (1C, CHS), 45.2 (1C, CH_2S), 36.6 (1C, CH), 27.8 (3C, OC(<u>C</u>H_3)$_3$). IR (neat): 2976, 1725, 1480, 1438, 1367, 1282, 1140, 739, 690 cm^{-1}. APCI-MS calcd for [$C_{22}H_{27}O_2S_2$, M + H]$^+$: 387.14, Found 387.13.



(–)-*tert*-Butyl (*S*)-2-azido-2-(1-vinylcyclopentyl)acetate, 8t: Colorless semi-oil, TLC R_f = 0.60 (Hexane/EtOAc = 30:1, v/v), 88% yield, 92% ee (ee value was determined by transformation to compound **S11t**). $[\alpha]_D^{24}$ –42.0 (*c* 0.13, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83 (dd, J_1 = 17.5 Hz and J_2 = 10.5 Hz, 1H, CH=), 5.16 (d, J = 10.5 Hz, 1H, 1/2(=CH_2)), 5.09 (d, J = 17.5 Hz, 1H, 1/2(=CH_2)), 3.69 (s, 1H, CHN_3), 1.87–1.82 (m, 1H, 1/2CH_2), 1.75–1.72 (m, 1H, 1/2CH_2), 1.69–1.58 (m, 6H, 3CH_2), 1.49 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0 (1C, C=O), 140.2 (1C, CH=), 114.9 (1C, =CH_2), 82.8 (1C, O<u>C</u>(CH_3)$_3$), 70.1 (1C, CHN_3), 52.9 (1C, C), 34.6 (1C, CH_2), 34.5 (1C, CH_2), 28.1 (3C, OC(<u>C</u>H_3)$_3$), 23.6 (1C, CH_2), 23.2 (1C, CH_2). IR (neat): 2979, 2933, 2107, 1727, 1673, 1618, 1369, 1304, 1252, 1143, 846, 784 cm^{-1}. APCI-MS calcd for [$C_{13}H_{22}N_3O_2$, M + H]$^+$: 252.17, Found 252.18.

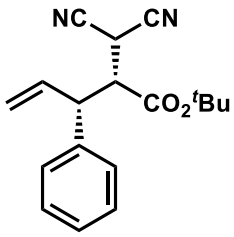


(–)-*tert*-Butyl (*S*)-2-azido-2-(1-vinylcyclohexyl)acetate, 8u: Colorless semi-oil, TLC R_f = 0.75 (Hexane/EtOAc = 30:1, v/v), 92% yield, 85% ee (ee value was determined by transformation to compound **S11u**). $[\alpha]_D^{24}$ –34.0 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.68 (dd, J_1 = 17.5 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.29 (d, J = 11.0 Hz, 1H, 1/2(=CH_2)), 5.12 (dd, J = 18.0 Hz, 1H, 1/2(=CH_2)), 3.64 (s, 1H, CHN_3), 1.70–1.40 (m, 10H, 5CH_2), 1.49 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6 (1C, C=O), 140.4 (1C, CH=), 116.9 (1C, =CH_2), 82.7 (1C, O$\underline{C}(CH_3)_3$), 70.2 (1C, CHN_3), 44.1 (1C, C), 32.8 (1C, CH_2), 32.3 (1C, CH_2), 28.1 (3C, OC($\underline{C}H_3)_3$), 26.0 (1C, CH_2), 21.8 (2C, 2CH_2). IR (neat): 2930, 2852, 2106, 1733, 1369, 1259, 1152, 920, 844, 668 cm^{-1}. APCI-MS calcd for $[C_{14}H_{24}N_3O_2, M + H]^+$: 266.19, Found 266.20.

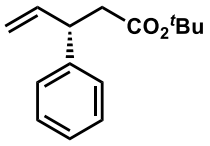


(–)-*tert*-Butyl (*S*)-2-azido-2-(1-vinylcycloheptyl)acetate, 8v: Colorless semi-oil, TLC R_f = 0.75 (Hexane/EtOAc = 30:1, v/v), 90% yield, 91% ee (ee value was determined by transformation to compound **S11v**). $[\alpha]_D^{24}$ –22.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (dd, J_1 = 17.6 Hz and J_2 = 10.8 Hz, 1H, CH=), 5.18 (dd, J_1 = 10.8 Hz and J_2 = 0.8 Hz, 1H, 1/2(=CH_2)), 5.09 (dd, J_1 = 17.6 Hz and J_2 = 0.8 Hz, 1H, 1/2(=CH_2)), 3.61 (s, 1H, CHN_3), 1.84–1.66 (m, 4H, 2CH_2), 1.60–1.52 (m, 4H, 2CH_2), 1.49 (s, 9H, $C(CH_3)_3$), 1.48–1.43 (m, 4H, 2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8 (1C, C=O), 142.1 (1C, CH=), 114.7 (1C, =CH_2), 82.8 (1C, O$\underline{C}(CH_3)_3$), 70.4 (1C, CHN_3), 47.1 (1C, C), 34.7 (1C, CH_2), 34.0 (1C, CH_2), 30.1 (1C, CH_2), 30.0 (1C, CH_2), 28.1 (3C, OC($\underline{C}H_3)_3$), 22.5 (1C, CH_2), 22.4 (2C, 2CH_2). IR (neat): 2926, 2857, 2106, 1733, 1369,

1258, 1150, 918, 845, 668 cm^{-1}. APCI-MS calcd for $[C_{15}H_{26}N_3O_2, M + H]^+$: 280.20, Found 280.20.

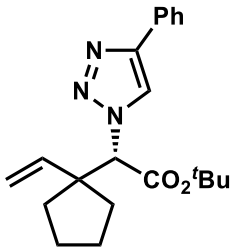


(+)-*tert*-Butyl (2*R*, 3*R*)-2-(dicyanomethyl)-3-phenylpent-4-enoate, 9a: White solid, mp: 115–116 °C, TLC R_f = 0.45 (Hexane/EtOAc = 10:1, v/v), 74% yield, 96% ee. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 210 nm UV detecter, t_R= 6.79 min (major) and t_R= 7.70 min (minor). $[\alpha]_D^{24}$ +24.0 (*c* 0.30, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.36 (m, 2H, ArH), 7.35–7.30 (m, 1H, ArH), 7.28–7.24 (m, 2H, ArH), 6.10–6.00 (m, 1H, =CH), 5.30–5.20 (m, 2H, $=CH_2$), 3.79 (t, J = 9.5 Hz, 1H, ArCH), 3.53 (d, J = 6.0 Hz, 1H, $CH(CN)_2$), 3.16 (dd, J_1 = 10.0 Hz and J_2 = 6.0 Hz, 1H, CH), 1.48 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2 (1C, C=O), 138.1 (1C, ArC), 135.4 (1C, =CH), 129.6 (2C, ArC), 128.3 (1C, ArC), 127.6 (2C, ArC), 118.9 (1C, $=CH_2$), 111.3 (1C, CN), 110.6 (1C, CN), 84.3 (1C, $O\underline{C}(CH_3)_3$), 51.4 (1C, CH), 50.4 (1C, CH), 27.8 (3C, $OC(\underline{C}H_3)_3$), 24.1 (1C, $CH(CN)_2$). IR (neat): 2983, 2906, 2256, 1716, 1370, 1250, 1151, 931, 704 cm^{-1}. APCI-MS calcd for $[C_{18}H_{21}N_2O_2, M + H]^+$: 297.16, Found 297.16.

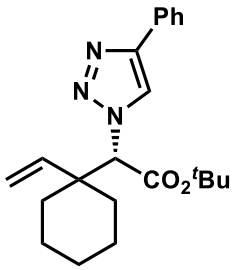


(+)-*tert*-Butyl (*S*)-3-phenylpent-4-enoate, 10a: Colorless semi-oil, TLC R_f = 0.55 (Hexane/EtOAc = 30:1, v/v), 85% yield, 93% ee. HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.5 mL/min, 210 nm UV detecter, t_R= 9.54 min (minor) and t_R= 11.30 min (major). $[\alpha]_D^{24}$ +2.4 (*c* 0.33, CH_2Cl_2).

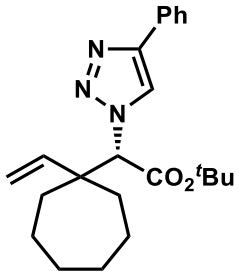
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.27 (m, 2H, ArH), 7.23–7.18 (m, 3H, ArH), 6.02–5.92 (m, 1H, =CH), 5.09–5.03 (m, 2H, $=CH_2$), 3.81 (q, J = 7.5 Hz, 1H, CH), 2.70–2.58 (m, 2H, CH_2), 1.35 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2 (1C, C=O), 142.5 (1C, ArC), 140.5 (1C, =CH), 128.4 (2C, ArC), 127.6 (2C, ArC), 126.5 (1C, ArC), 114.5 (1C, $=CH_2$), 80.4 (1C, $O\underline{C}(CH_3)_3$), 45.9 (1C, CH), 41.4 (1C, CH_2), 28.0 (3C, $OC(\underline{C}H_3)_3$). IR (neat): 2978, 1729, 1367, 1257, 1148, 917, 754, 700 cm^{-1}. APCI-MS calcd for $[C_{15}H_{21}O_2, M + H]^+$: 233.15, Found 233.15.



(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcyclopentyl)acetate, S11t: Colorless semi-oil, TLC R_f = 0.50 (Hexane/EtOAc = 8:1, v/v), 86% yield, 92% ee. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 0.8 mL/min, 254 nm UV detecter, t_R= 14.69 min (minor) and t_R= 15.39 min (major). $[\alpha]_D^{24}$ +22.0 (*c* 0.30, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H, NCH=), 7.88–7.80 (m, 2H, ArH), 7.42 (t, J = 7.5 Hz, 2H, ArH), 7.32 (t, J = 7.5 Hz, 1H, ArH), 5.90 (dd, J_1 = 17.5 Hz and J_2 = 10.5 Hz, 1H, CH=), 5.38 (s, 1H, CHN), 5.30 (d, J = 11.0 Hz, 1H, 1/2(=CH_2)), 5.03 (d, J = 17.5 Hz, 1H, 1/2(=CH_2)), 1.94–1.83 (m, 2H, CH_2), 1.77–1.70 (m, 1H, 1/2CH_2), 1.68–1.64 (m, 1H, 1/2CH_2), 1.58–1.40 (m, 13H, 2CH_2 + $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (1C, C=O), 147.0 (1C, =C), 138.9 (1C, CH=), 130.8 (1C, ArC), 128.7 (2C, ArC), 127.9 (1C, NCH=), 125.7 (2C, ArC), 120.2 (1C, ArC), 116.8 (1C, $=CH_2$), 83.5 (1C, $O\underline{C}(CH_3)_3$), 70.5 (1C, CHN), 53.2 (1C, C), 36.5 (1C, CH_2), 33.2 (1C, CH_2), 28.0 (3C, $OC(\underline{C}H_3)_3$), 23.3 (1C, CH_2), 22.5 (1C, CH_2). IR (neat): 2972, 1736, 1369, 1240, 1154, 1074, 1041, 922, 866 cm^{-1}. APCI-MS calcd for $[C_{21}H_{28}N_3O_2, M + H]^+$: 354.22, Found 354.22.



(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcyclohexyl)acetate, S11u: Colorless semi-oil, TLC R_f = 0.55 (Hexane/EtOAc = 8:1, v/v), 90% yield, 85% ee. HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 254 nm UV detecter, t_R= 7.39 min (major) and t_R= 9.46 min (minor). $[\alpha]_D^{24}$ +19.0 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H, NCH=), 7.87–7.82 (m, 2H, ArH), 7.42 (t, *J* = 7.5 Hz, 2H, ArH), 7.32 (t, *J* = 7.5 Hz, 1H, ArH), 5.76 (dd, J_1 = 17.5 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.47 (brs, 1H, CHN), 5.40 (d, *J* = 11.0 Hz, 1H, 1/2(=CH_2)), 4.98 (d, *J* = 18.0 Hz, 1H, 1/2(=CH_2)), 1.82–1.62 (m, 4H, 2CH_2), 1.52–1.46 (m, 11H, CH_2 + $C(CH_3)_3$), 1.42–1.27 (m, 4H, 2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (1C, C=O), 146.8 (1C, =C), 139.7 (1C, CH=), 130.8 (1C, ArC), 128.8 (2C, ArC), 127.9 (1C, NCH=), 125.6 (2C, ArC), 120.5 (1C, ArC), 118.3 (1C, =CH_2), 83.5 (1C, O$\underline{C}(CH_3)_3$), 70.2 (1C, CHN), 44.2 (1C, C), 34.5 (1C, CH_2), 31.5 (1C, CH_2), 28.0 (3C, OC($\underline{C}H_3)_3$), 25.7 (1C, CH_2), 21.8 (1C, CH_2), 21.4 (1C, CH_2). IR (neat): 2934, 2857, 1735, 1458, 1369, 1153, 1073, 1042, 765, 694 cm^{-1}. APCI-MS calcd for $[C_{22}H_{30}N_3O_2, M + H]^+$: 368.23, Found 368.23.

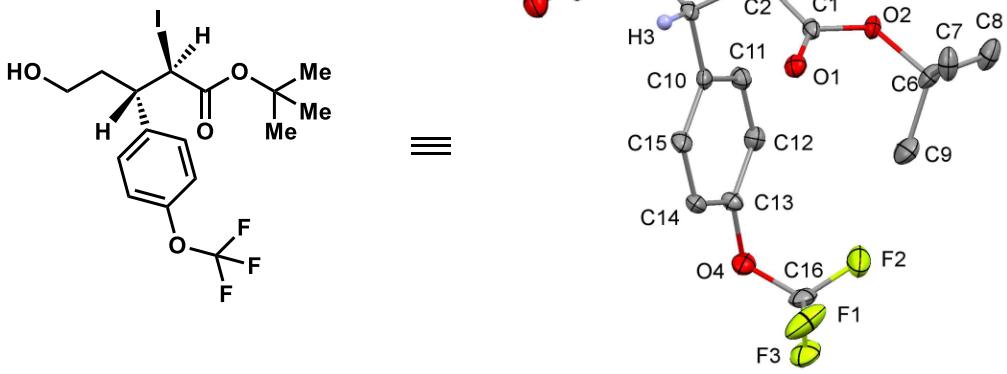


(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcycloheptyl)acetate, S11v: Colorless semi-oil, TLC R_f = 0.60 (Hexane/EtOAc = 8:1, v/v), 88% yield, 91% ee.

HPLC conditions: Chiralcel AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 254 nm UV detecter, t_R= 7.21 min (major) and t_R= 9.34 min (minor). $[\alpha]_D^{24}$ +13.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H, NCH=), 7.84 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (t, *J* = 8.0 Hz, 2H, ArH), 7.32 (t, *J* = 7.5 Hz, 1H, ArH), 5.89 (dd, J_1 = 17.5 Hz and J_2 = 11.0 Hz, 1H, CH=), 5.38 (s, 1H, CHN), 5.29 (d, *J* = 11.0 Hz, 1H, 1/2(=CH_2)), 4.97 (d, *J* = 17.5 Hz, 1H, 1/2(=CH_2)), 1.95–1.88 (m, 1H, 1/2CH_2), 1.77–1.71 (m, 1H, 1/2CH_2), 1.56–1.38 (m, 19H, 5CH_2 + $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (1C, C=O), 146.8 (1C, =C), 141.1 (1C, CH=), 130.8 (1C, ArC), 128.7 (2C, ArC), 127.9 (1C, NCH=), 125.6 (2C, ArC), 120.5 (1C, ArC), 116.2 (1C, =CH_2), 83.5 (1C, O$\underline{C}(CH_3)_3$), 70.4 (1C, CHN), 47.5 (1C, C), 36.0 (1C, CH_2), 32.7 (1C, CH_2), 30.2 (1C, CH_2), 30.1 (1C, CH_2), 28.0 (3C, OC($\underline{C}H_3)_3$), 22.1 (1C, CH_2), 22.0 (1C, CH_2). IR (neat): 2928, 2857, 1735, 1462, 1369, 1238, 1152, 1073, 1041, 922, 764, 695 cm^{-1}. APCI-MS calcd for $[C_{23}H_{32}N_3O_2, M + H]^+$: 382.25, Found 382.25.

9. X-Ray Diffraction Analysis of (2*R*, 3*S*)-6i

A sample of (2*R*, 3*S*)-**6i** was recrystallized from 10:1 Hexane:Et_2O (slow evaporation). The resulting crystals were suitable for X-ray diffraction and the structure was solved. This structure allowed the assignment of absolute configuration as shown. The relative configurations of all other [2,3]-rearrangement products were assigned by analogy. We thank Dr. Vincent Lynch (Manager of the X-ray Diffraction Lab at UT Austin) for the X-ray structural analysis. The CIF file is available as a separate file in the Supporting Information.



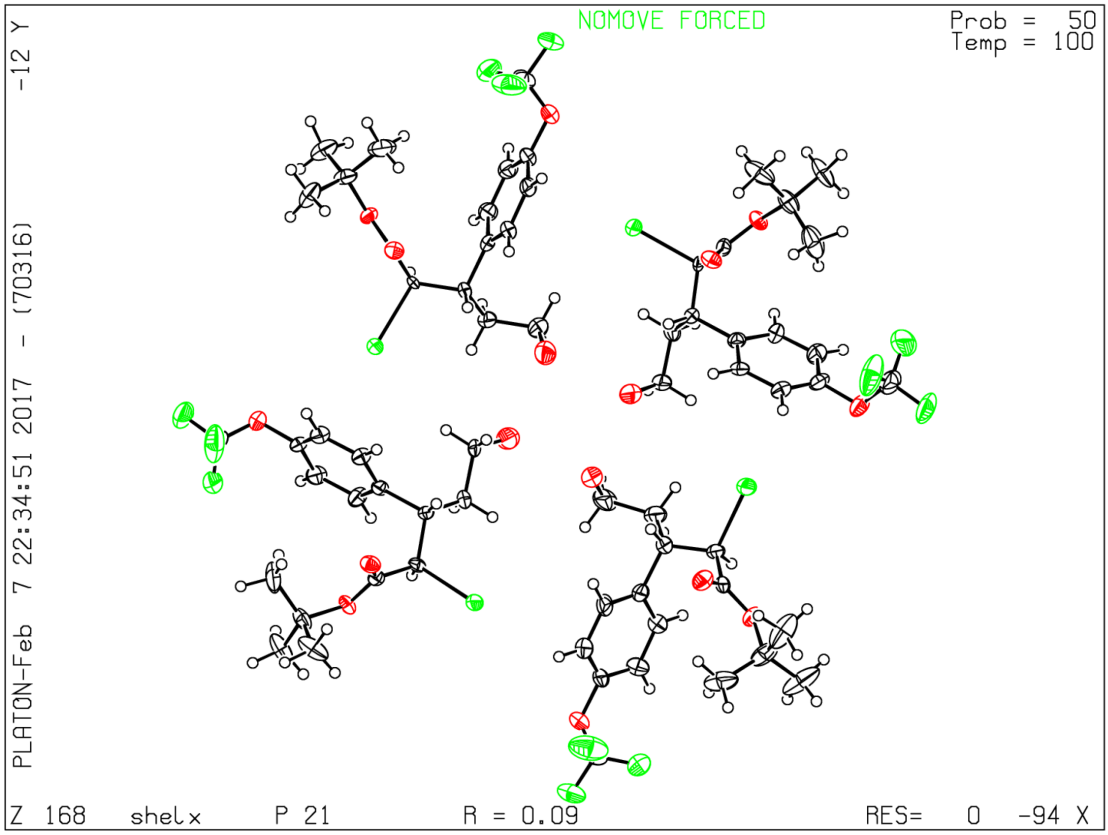


Table 1. Crystal data and structure refinement for 1.

Empirical formula	C16 H20 F3 I O4
Formula weight	460.22
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	monoclinic

Space group	P 21	
Unit cell dimensions	a = 26.5393(4) Å	α= 90°.
	b = 5.50860(10) Å	β= 90.6680(10)°.
	c = 26.7258(4) Å	γ = 90°.
Volume	3906.90(11) $Å^3$	
Z	8	
Density (calculated)	1.565 Mg/m^3	
Absorption coefficient	13.281 mm^{-1}	
F(000)	1824	
Crystal size	0.180 x 0.060 x 0.050 mm^3	
Theta range for data collection	2.333 to 76.039°.	
Index ranges	-32<=h<=33, -6<=k<=6, -33<=l<=33	
Reflections collected	66438	
Independent reflections	15936 [R(int) = 0.1101]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian and multi-scan	
Max. and min. transmission	1.00 and 0.348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15936 / 1 / 877	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0918, wR2 = 0.2359	
R indices (all data)	R1 = 0.0996, wR2 = 0.2476	
Absolute structure parameter	-0.025(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	5.911 and -1.237 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	8898(5)	6040(30)	9619(5)	28(3)
C2	8815(4)	4110(30)	9230(4)	24(2)
C3	8267(4)	4050(30)	9027(5)	28(3)
C4	8184(5)	1770(30)	8702(5)	35(3)
C5	7655(6)	1440(30)	8504(5)	39(3)

C6	9222(6)	6770(30)	10471(5)	36(3)
C7	9561(7)	8760(30)	10325(6)	46(4)
C8	9484(8)	5000(40)	10833(6)	49(4)
C9	8722(8)	7640(50)	10677(6)	57(5)
C10	7912(5)	4080(30)	9482(5)	29(3)
C11	7929(5)	2280(30)	9840(5)	33(3)
C12	7619(5)	2320(30)	10248(5)	33(3)
C13	7288(5)	4240(30)	10302(5)	27(3)
C14	7263(5)	6070(30)	9951(5)	32(3)
C15	7574(5)	5970(30)	9538(5)	35(3)
C16	7115(7)	5380(40)	11122(6)	44(4)
C17	5334(5)	3850(30)	8895(5)	25(2)
C18	5734(4)	1930(20)	8808(4)	21(2)
C19	5918(5)	1890(30)	8270(4)	27(3)
C20	6265(5)	-310(30)	8183(5)	35(3)
C21	6486(6)	-390(30)	7666(5)	36(3)
C22	4492(6)	4600(30)	9217(7)	40(4)
C23	4659(8)	6600(30)	9560(8)	53(5)
C24	4130(6)	2890(40)	9473(8)	56(5)
C25	4269(7)	5400(40)	8721(9)	62(6)
C26	5469(5)	1930(30)	7905(5)	27(3)
C27	5106(5)	120(30)	7918(5)	32(3)
C28	4697(6)	140(30)	7603(5)	38(3)
C29	4638(6)	2100(30)	7271(5)	34(3)
C30	4994(5)	3870(30)	7243(5)	30(3)
C31	5409(5)	3820(30)	7565(4)	30(3)
C32	3807(7)	3190(50)	7084(7)	57(5)
C33	6116(5)	2160(30)	5331(5)	31(3)
C34	6213(5)	210(30)	5731(4)	32(3)
C35	6759(5)	360(30)	5917(5)	37(3)
C36	6888(6)	-1640(40)	6289(5)	48(5)
C37	7389(6)	-1140(50)	6558(7)	57(5)
C38	5777(8)	2700(30)	4485(6)	50(4)
C39	6267(10)	3590(40)	4283(7)	64(6)
C40	5427(9)	4720(40)	4653(10)	73(7)

C41	5503(11)	1000(40)	4143(7)	78(8)
C42	7124(5)	290(30)	5464(5)	33(3)
C43	7088(5)	-1670(30)	5125(5)	36(3)
C44	7396(6)	-1680(30)	4714(6)	42(4)
C45	7742(5)	150(30)	4650(5)	35(3)
C46	7780(6)	2040(30)	4974(6)	39(3)
C47	7463(5)	2070(30)	5386(6)	41(4)
C48	7919(8)	1090(50)	3814(6)	57(5)
C49	9601(5)	9160(20)	6087(4)	23(2)
C50	9212(4)	7210(20)	6163(4)	21(2)
C51	9007(5)	7210(30)	6699(4)	25(3)
C52	8661(5)	5000(30)	6788(5)	34(3)
C53	8438(5)	5080(40)	7310(5)	41(4)
C54	10469(5)	9880(30)	5808(6)	36(3)
C55	10837(6)	8150(30)	5561(9)	55(5)
C56	10318(8)	11850(30)	5439(8)	54(5)
C57	10663(6)	10740(50)	6304(9)	60(6)
C58	9461(5)	7250(20)	7070(4)	24(3)
C59	9519(5)	9090(30)	7418(5)	32(3)
C60	9931(6)	9060(30)	7744(5)	34(3)
C61	10270(5)	7220(30)	7721(5)	33(3)
C62	10224(6)	5310(30)	7382(5)	34(3)
C63	9816(5)	5290(30)	7054(5)	33(3)
C64	11102(7)	8230(50)	7929(6)	54(5)
I1	9328(1)	4987(2)	8623(1)	35(1)
I2	6337(1)	2708(3)	9331(1)	39(1)
I3	5703(1)	1033(3)	6337(1)	44(1)
I4	8623(1)	7941(2)	5620(1)	35(1)
O1	8775(4)	8140(20)	9551(3)	31(2)
O2	9119(3)	5140(20)	10028(3)	28(2)
O3	7537(5)	3400(30)	8189(5)	50(3)
O4	6954(4)	4280(20)	10707(4)	37(2)
O5	5400(4)	5933(19)	8760(4)	29(2)
O6	4935(3)	2990(20)	9115(3)	28(2)
O7	6753(4)	1850(30)	7580(4)	49(3)

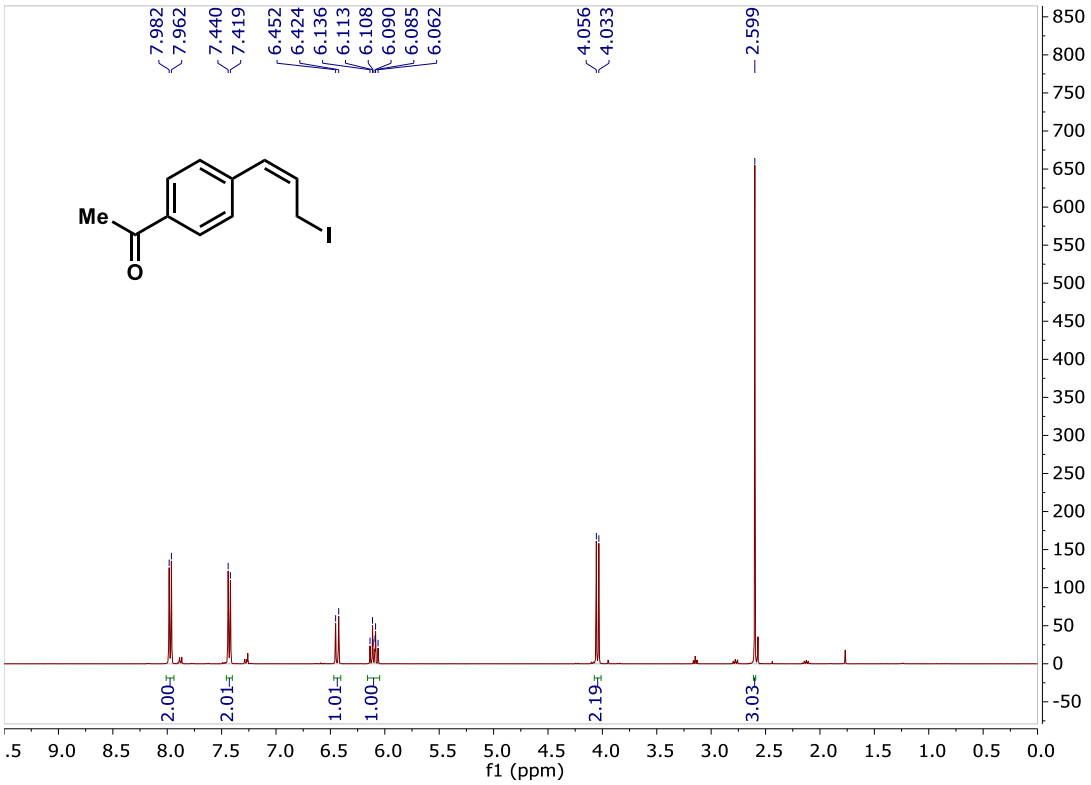
O8	4241(4)	2090(20)	6924(4)	39(3)
O9	6233(4)	4220(20)	5390(4)	36(2)
O10	5896(4)	1200(20)	4937(3)	33(2)
O11	7378(5)	1250(40)	6792(5)	72(5)
O12	8077(4)	-30(30)	4242(4)	43(3)
O13	9542(4)	11236(18)	6215(3)	29(2)
O14	10016(3)	8259(17)	5883(3)	26(2)
O15	8146(5)	2940(30)	7370(4)	61(4)
O16	10678(4)	7110(20)	8068(4)	38(2)
F1	7185(6)	7760(30)	11058(4)	80(5)
F2	7526(5)	4470(40)	11310(4)	86(6)
F3	6757(4)	5150(30)	11467(4)	57(3)
F4	3889(5)	5590(30)	7164(7)	89(6)
F5	3626(5)	2160(40)	7490(5)	94(7)
F6	3471(4)	3030(30)	6727(5)	67(3)
F7	7501(5)	150(50)	3636(4)	98(7)
F8	7875(7)	3460(30)	3879(5)	86(5)
F9	8280(5)	670(30)	3481(4)	74(5)
F10	11042(5)	10620(30)	7868(7)	83(5)
F11	11449(4)	7930(30)	8286(4)	63(3)
F12	11289(4)	7320(40)	7512(4)	91(7)

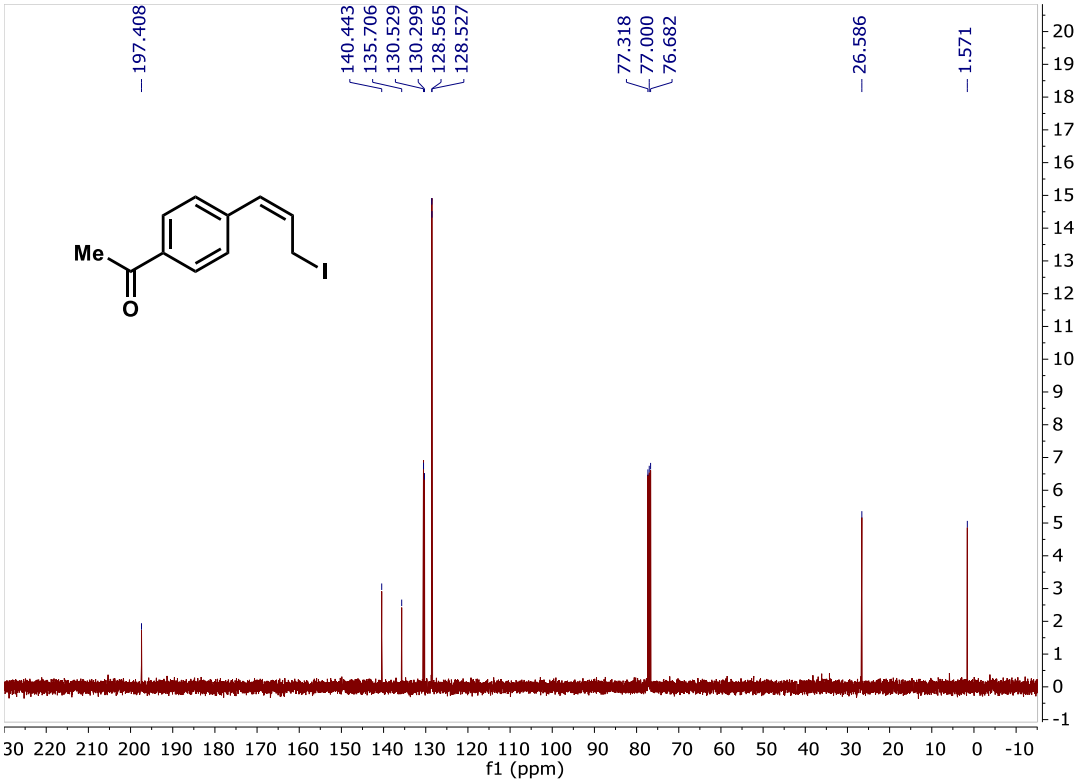
10. References

[1] B. Xu, U. K. Tambar, *J. Am. Chem. Soc.* **2016**, *138*, 12073−12076.
[2] P. Szcześniak, M. Pieczykolan, S. Stecko, *J. Org. Chem.* **2016**, *81*, 1057–1074.

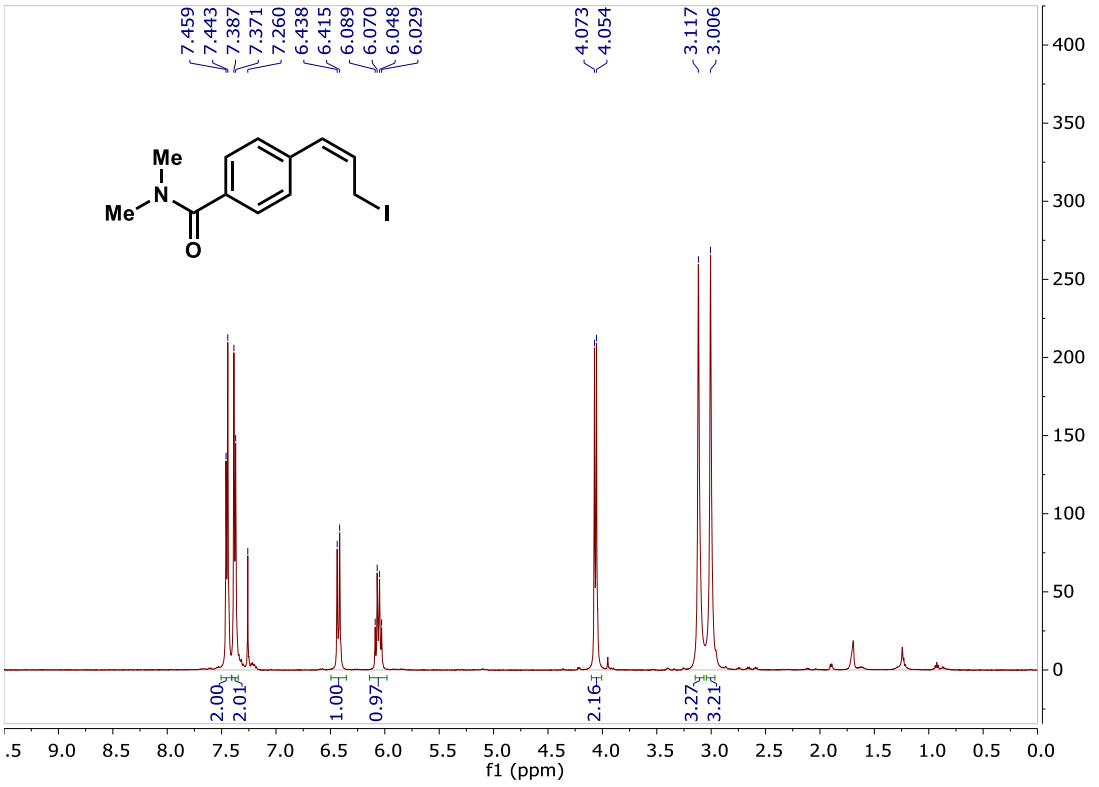
11. NMR Spectra

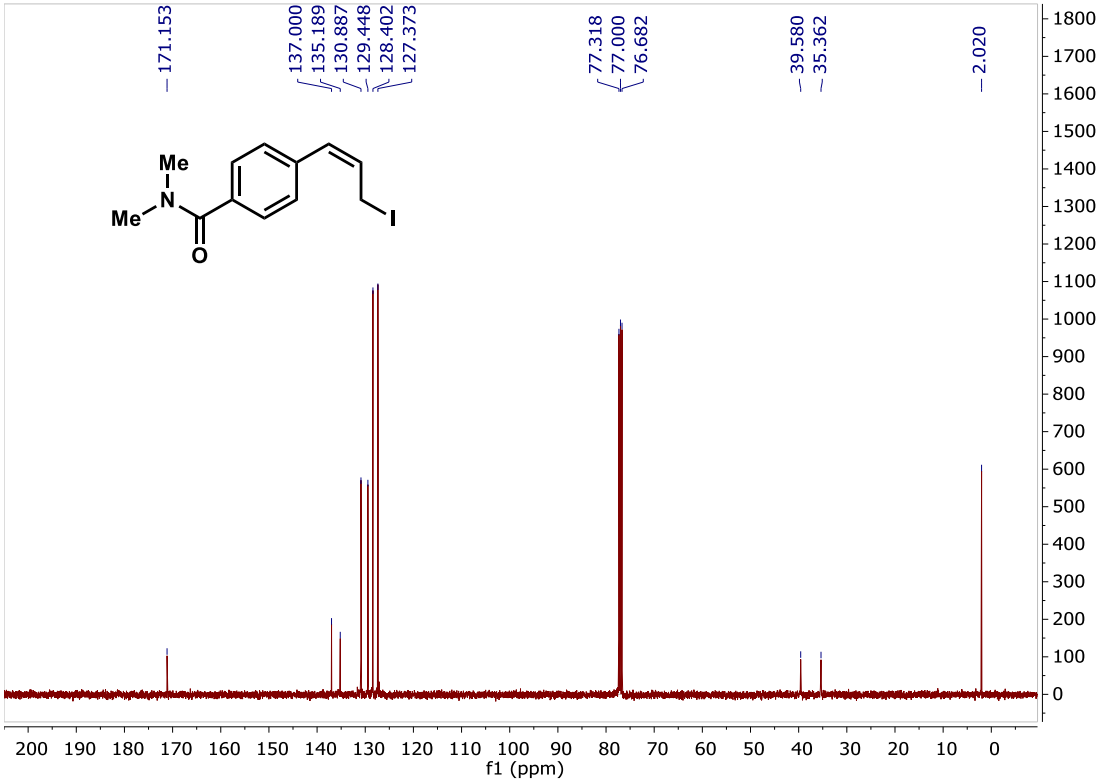
(*Z*)-1-(4-(3-iodoprop-1-en-1-yl)phenyl)ethan-1-one, 1e



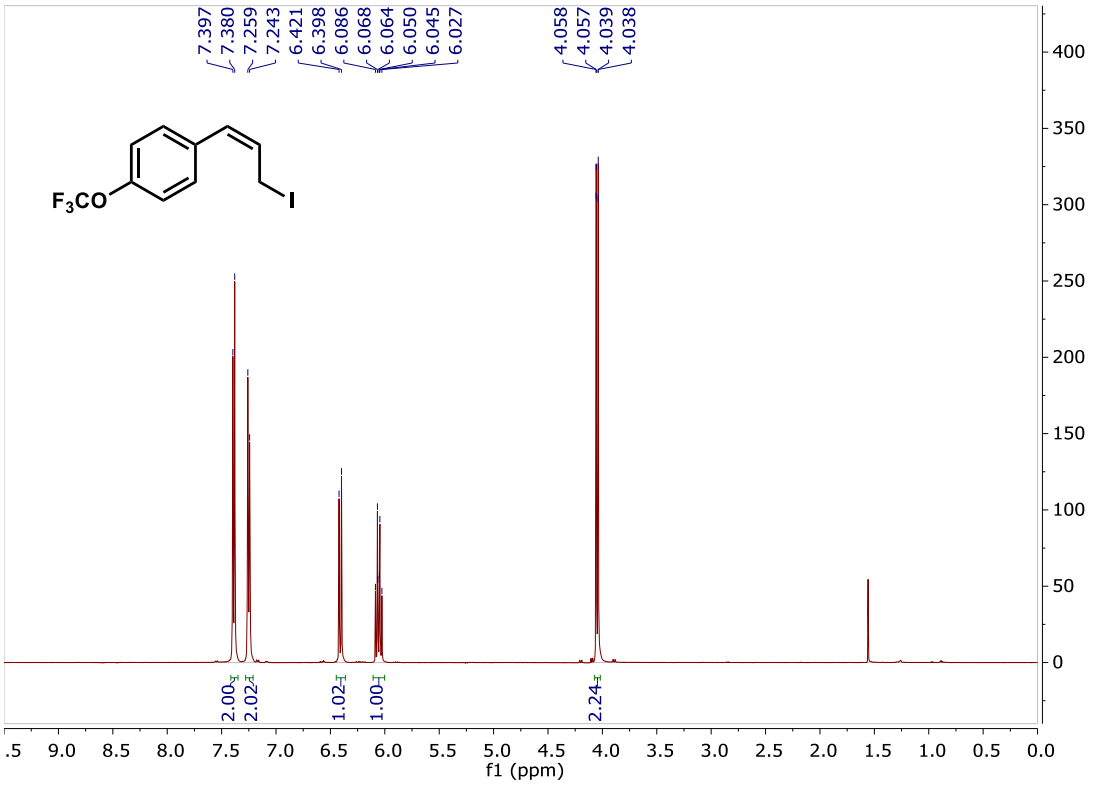


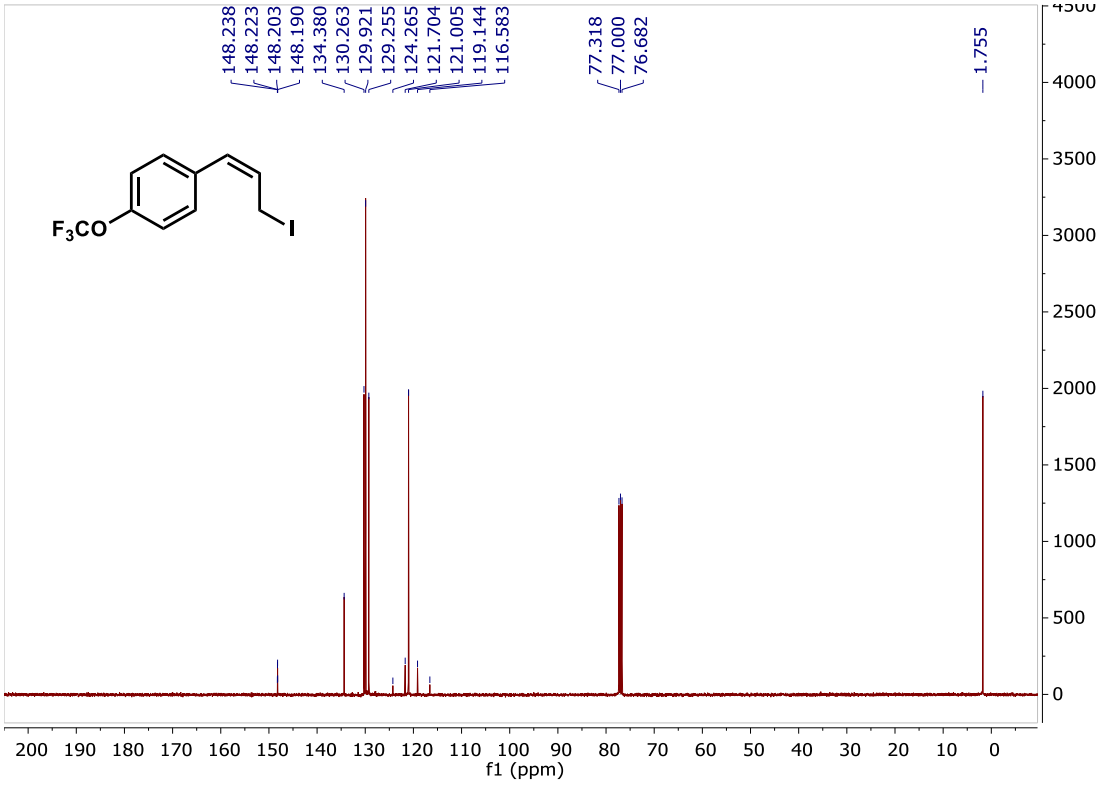
(*Z*)-4-(3-Iodoprop-1-en-1-yl)-*N*,*N*-dimethylbenzamide, 1g



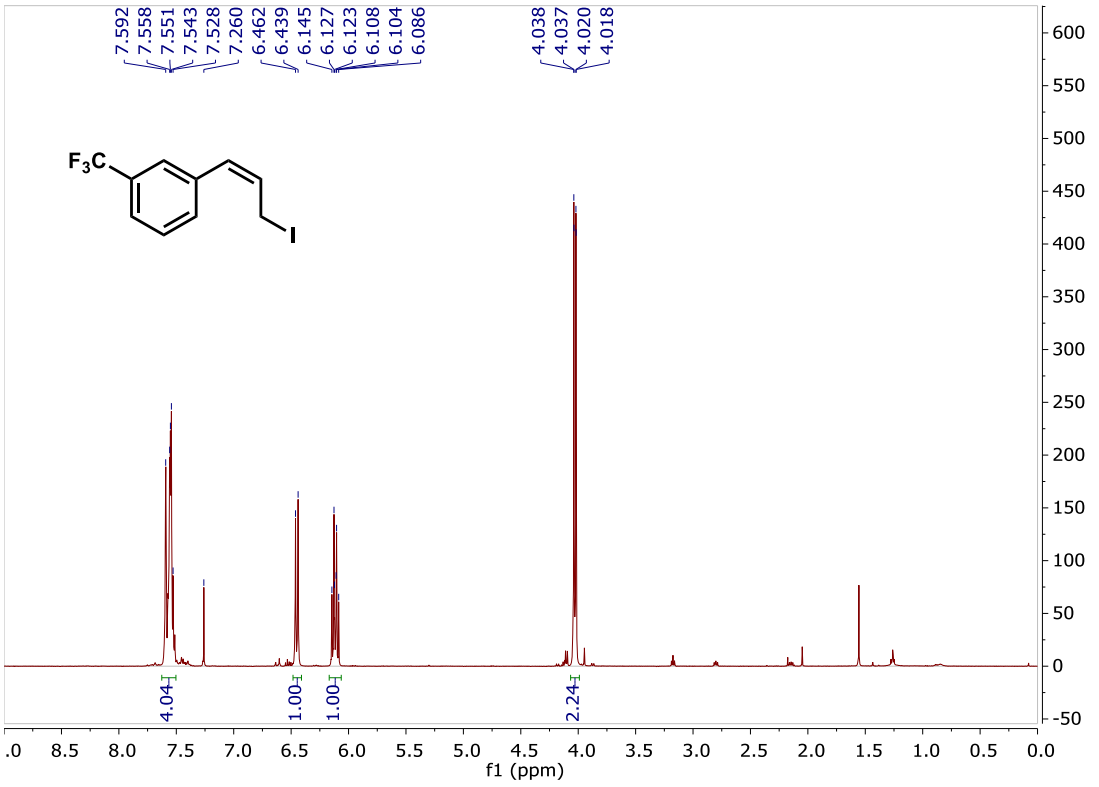


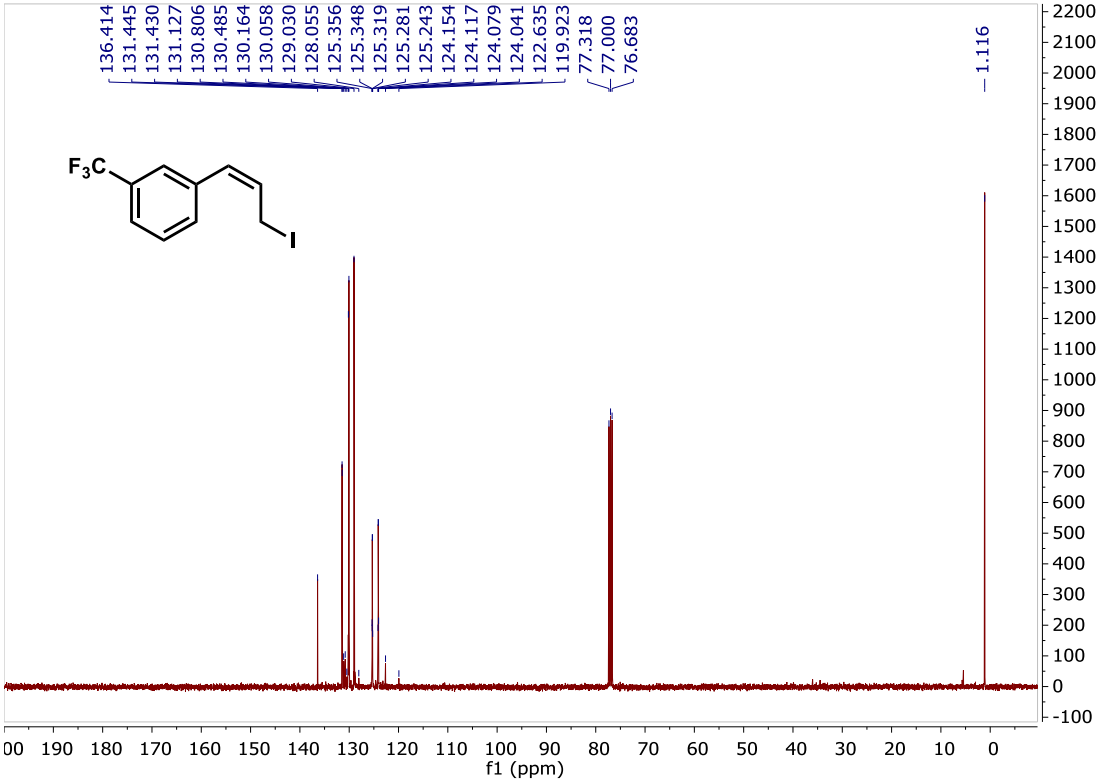
(*Z*)-1-(3-iodoprop-1-en-1-yl)-4-(trifluoromethoxy)benzene, 1i



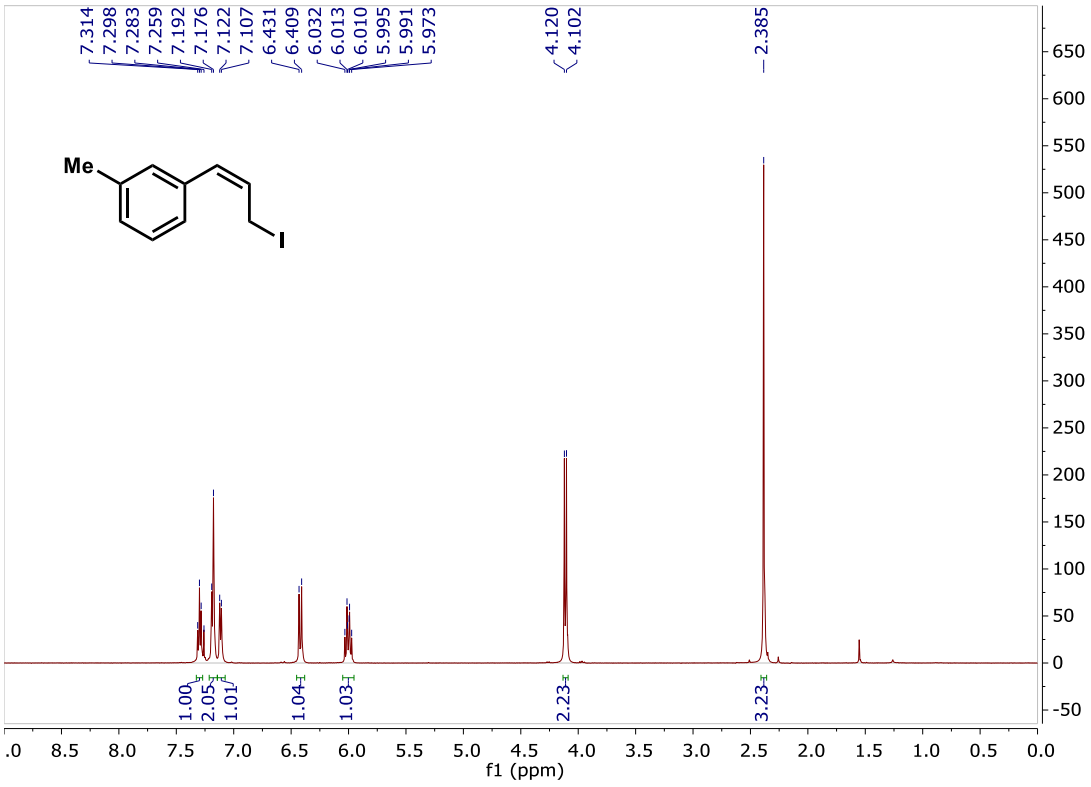


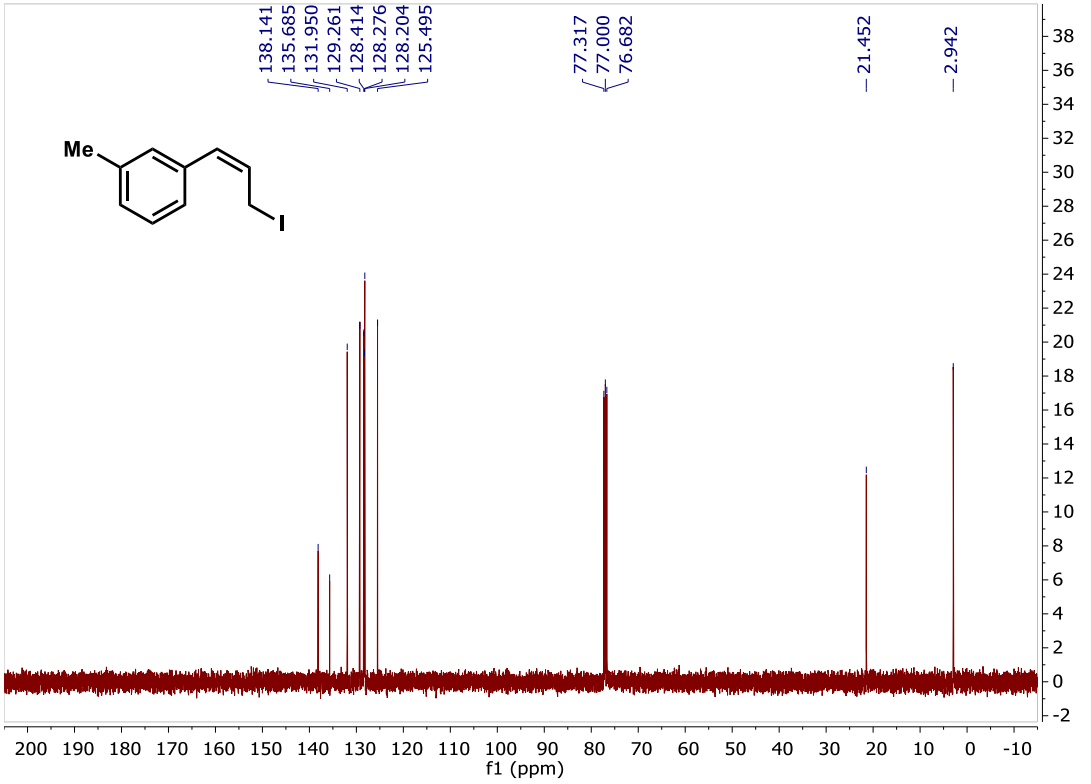
(*Z*)-1-(3-iodoprop-1-en-1-yl)-3-(trifluoromethyl)benzene, 1j



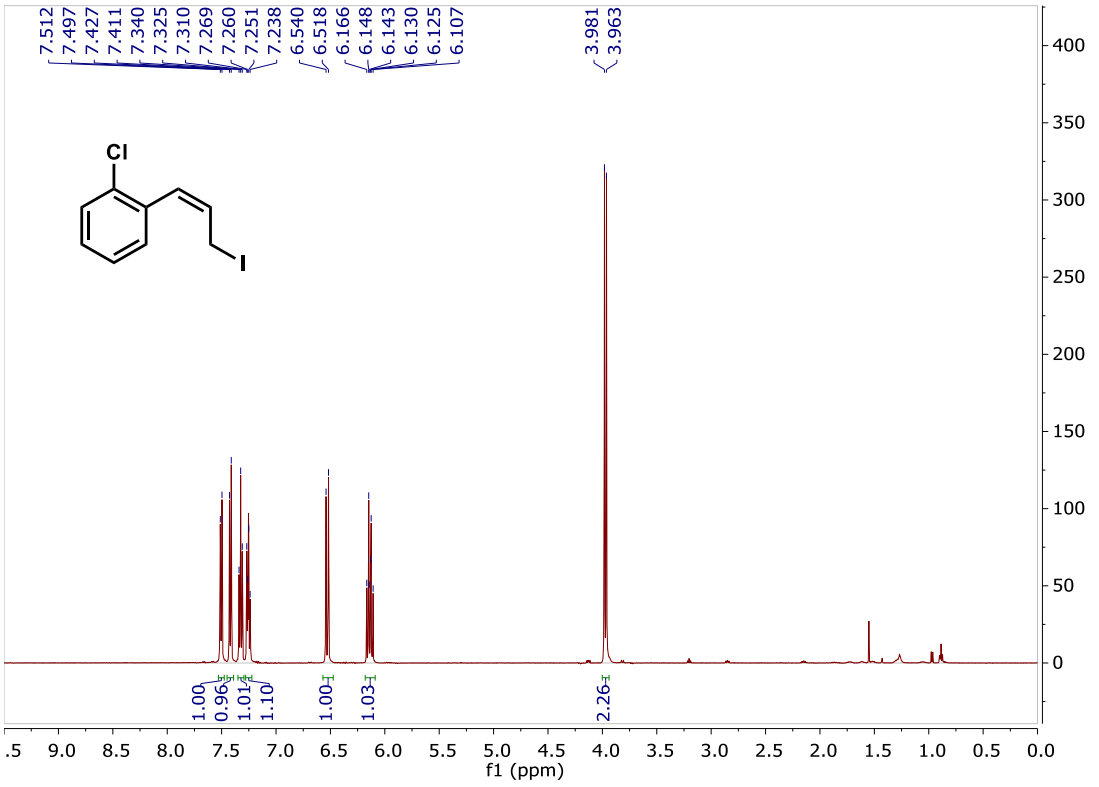


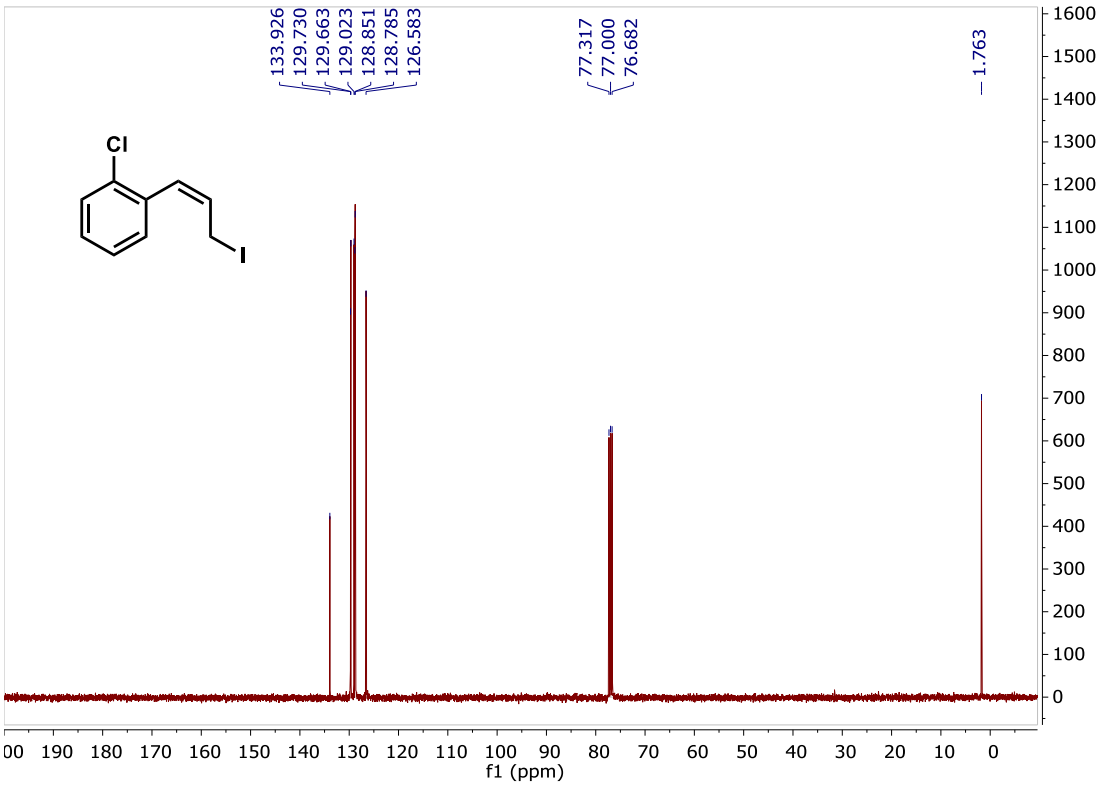
(*Z*)-1-(3-Iodoprop-1-en-1-yl)-3-methylbenzene, 1k



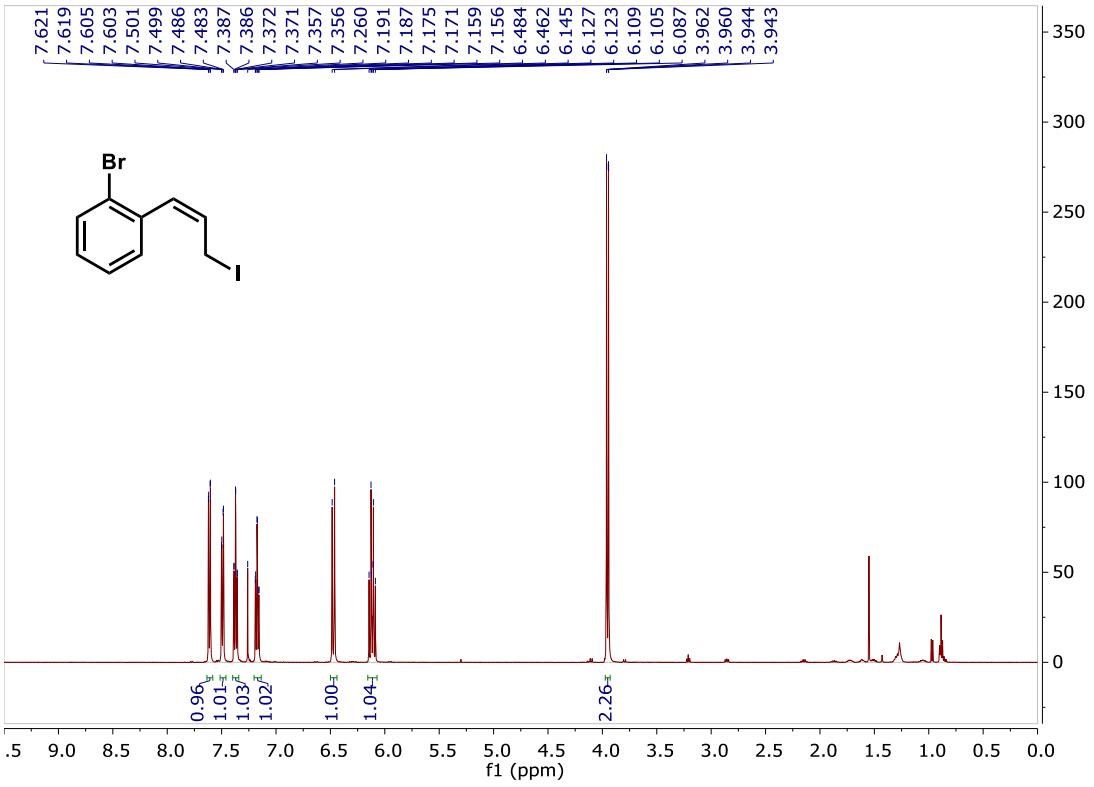


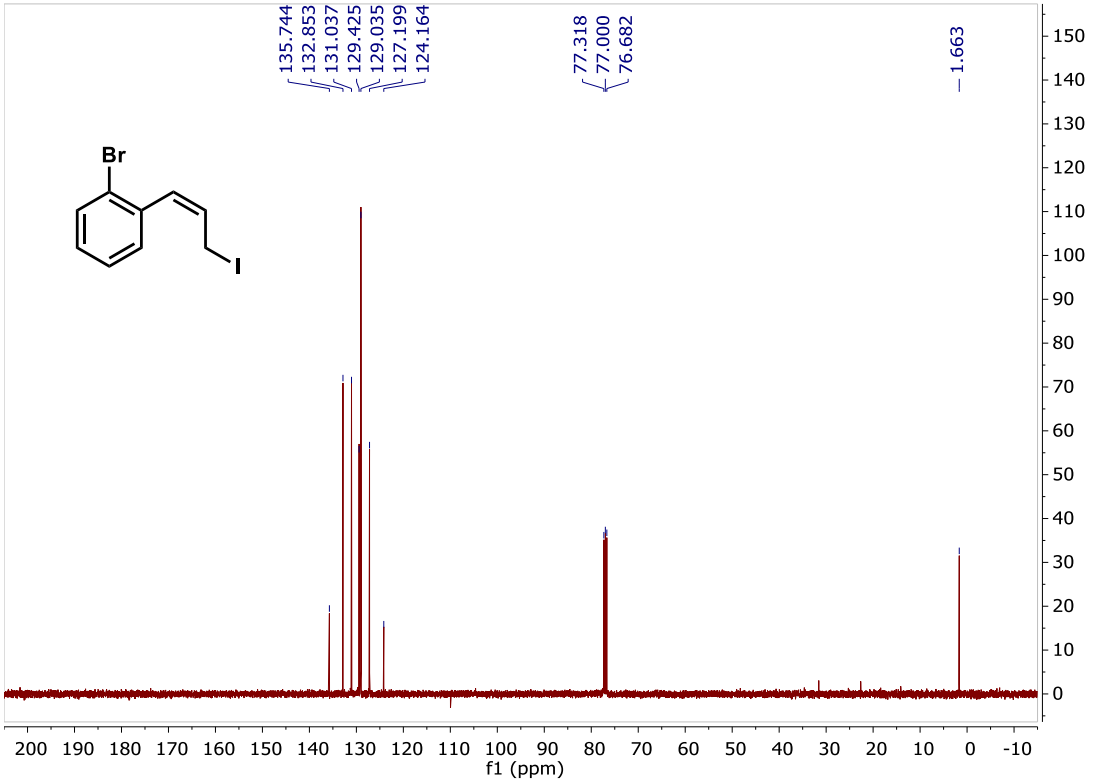
(*Z*)-1-Chloro-2-(3-iodoprop-1-en-1-yl)benzene, 1l



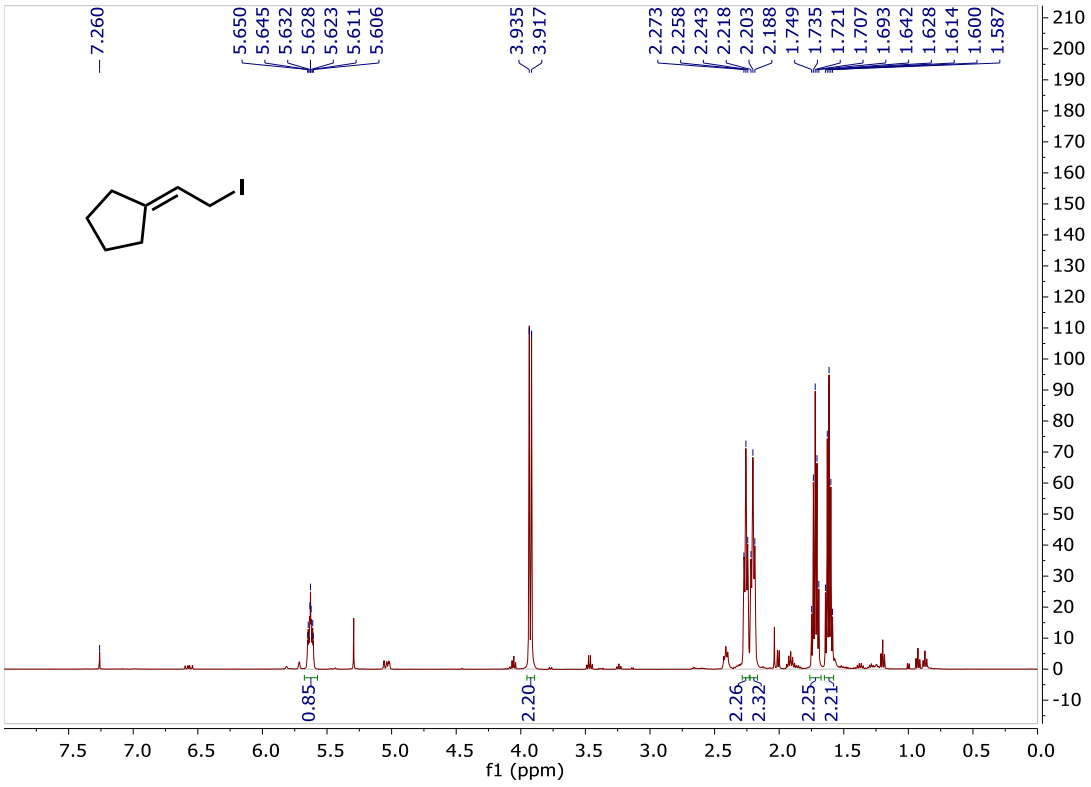


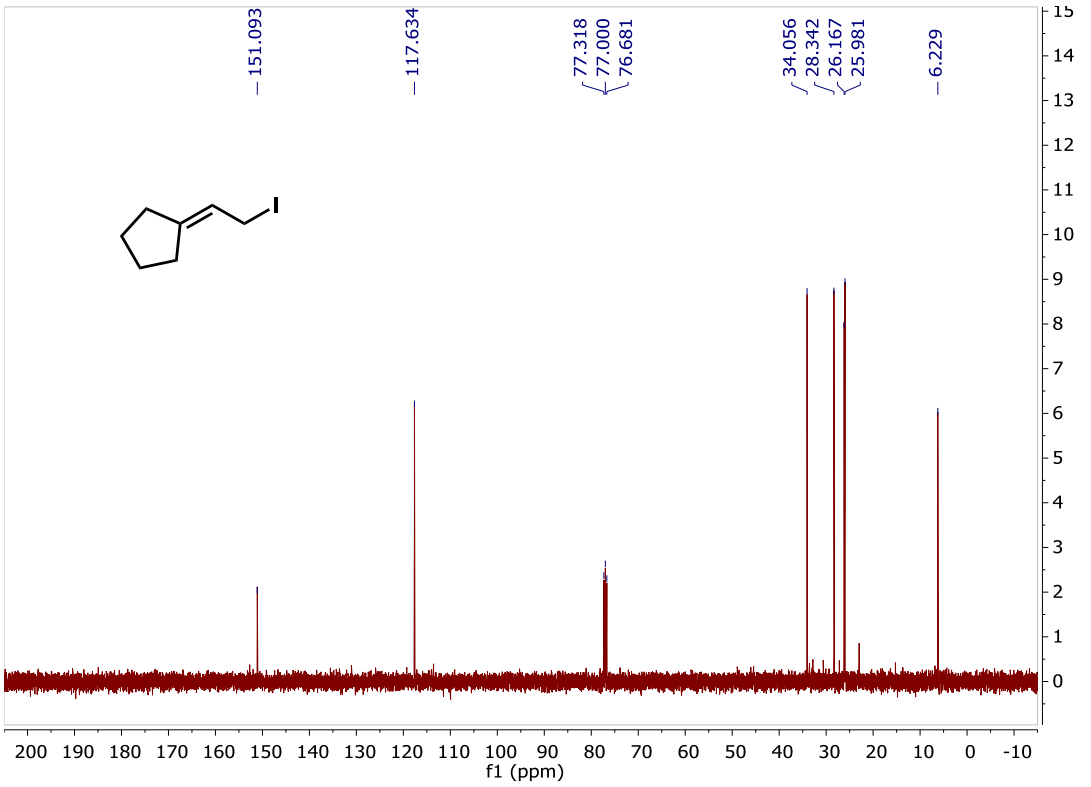
(*Z*)-1-Bomo-2-(3-iodoprop-1-en-1-yl)benzene, 1m



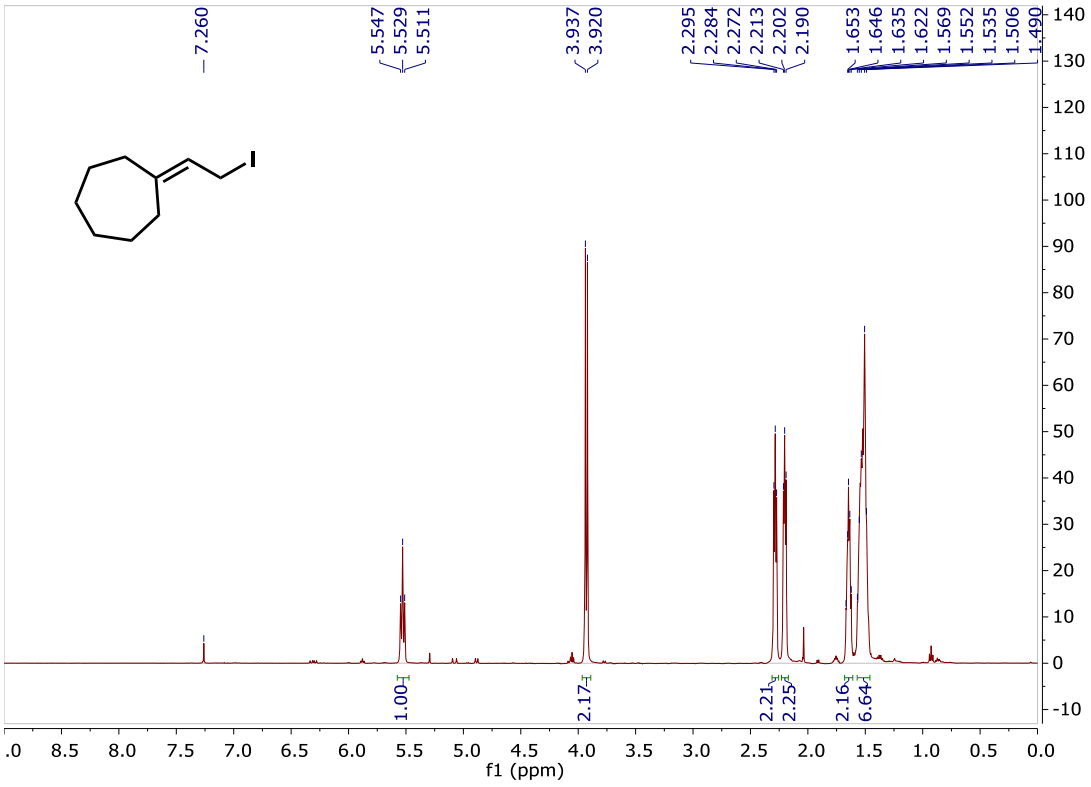


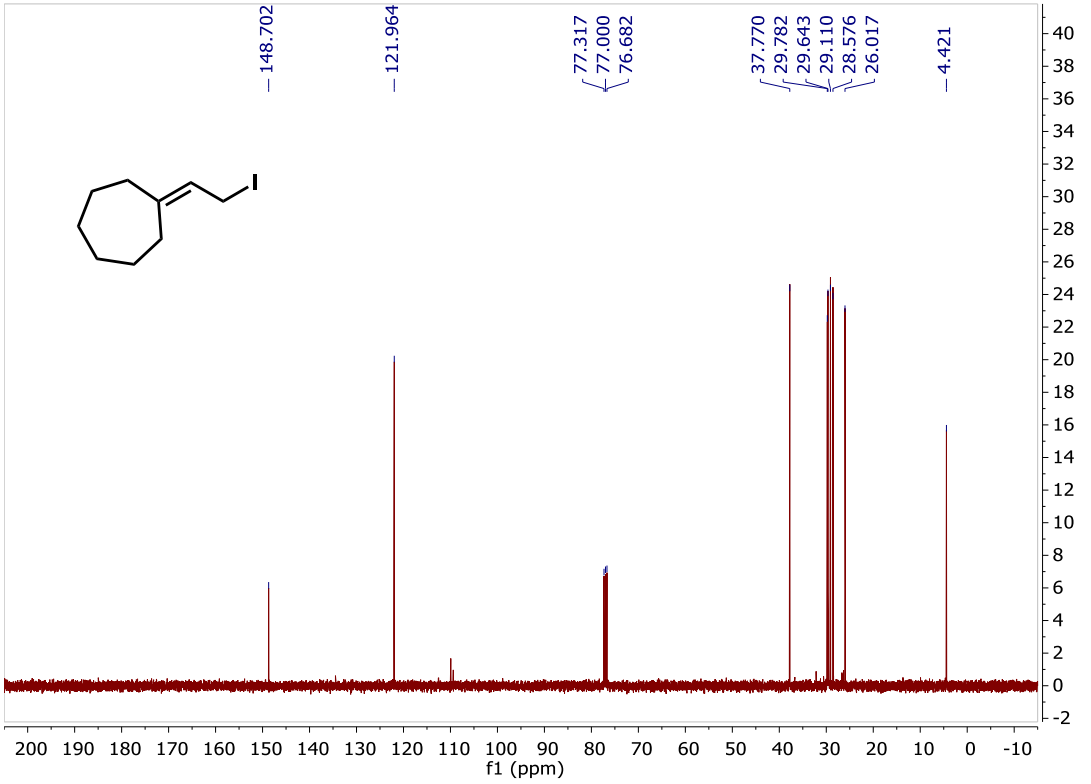
(2-Iodoethylidene)cyclopentane, 1t



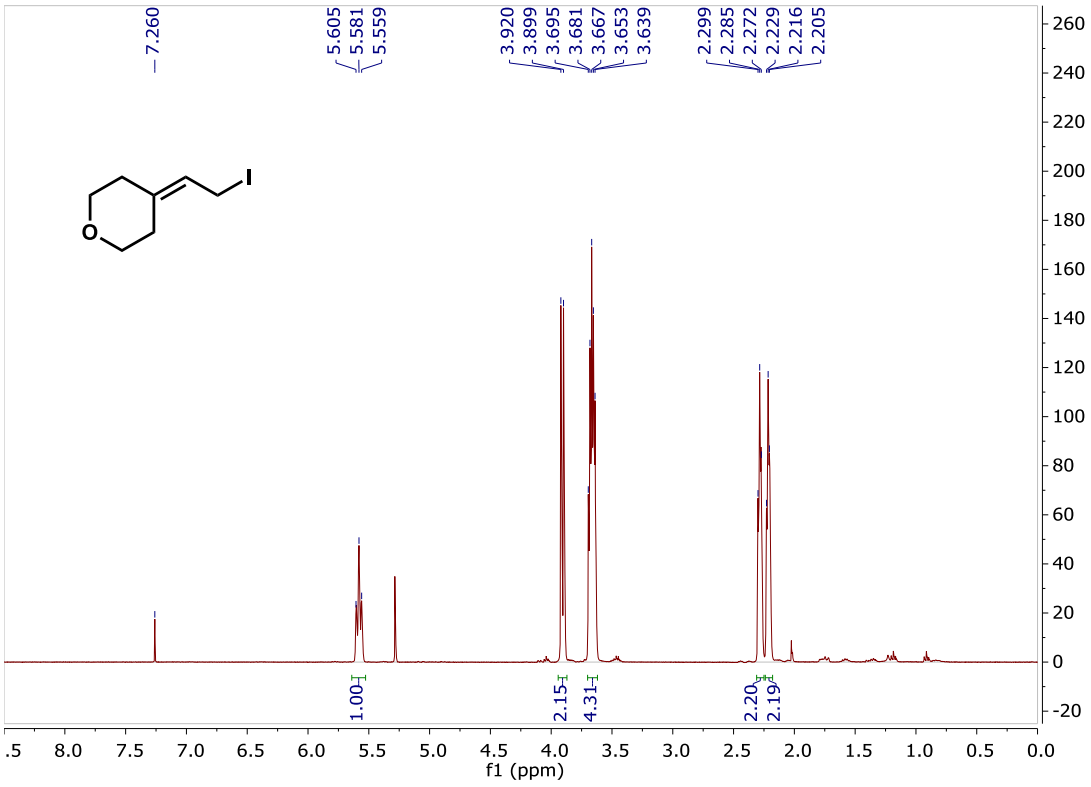


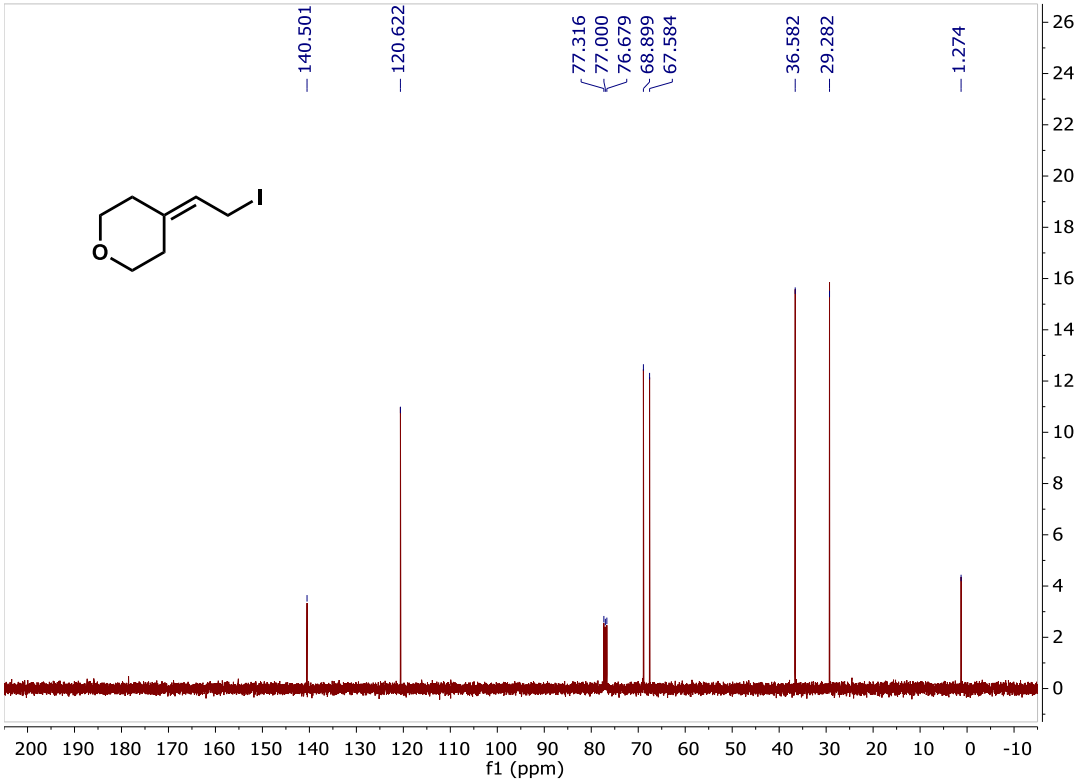
(2-Iodoethylidene)cycloheptane, 1v



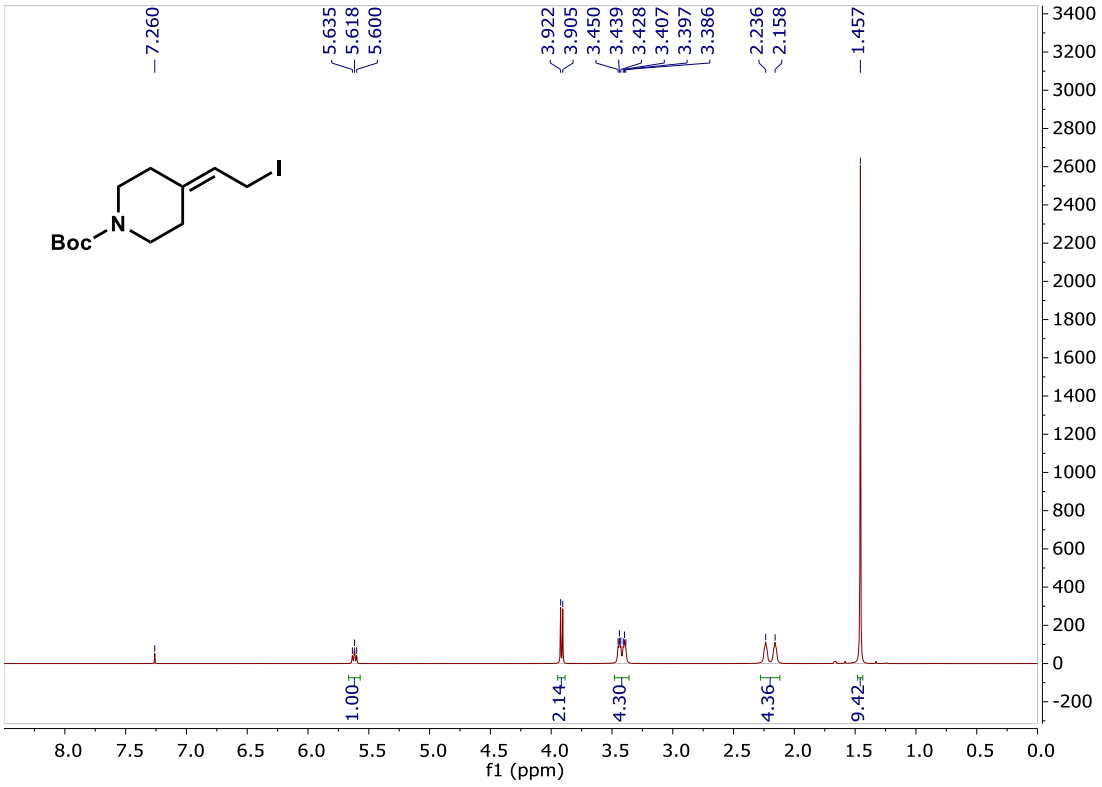


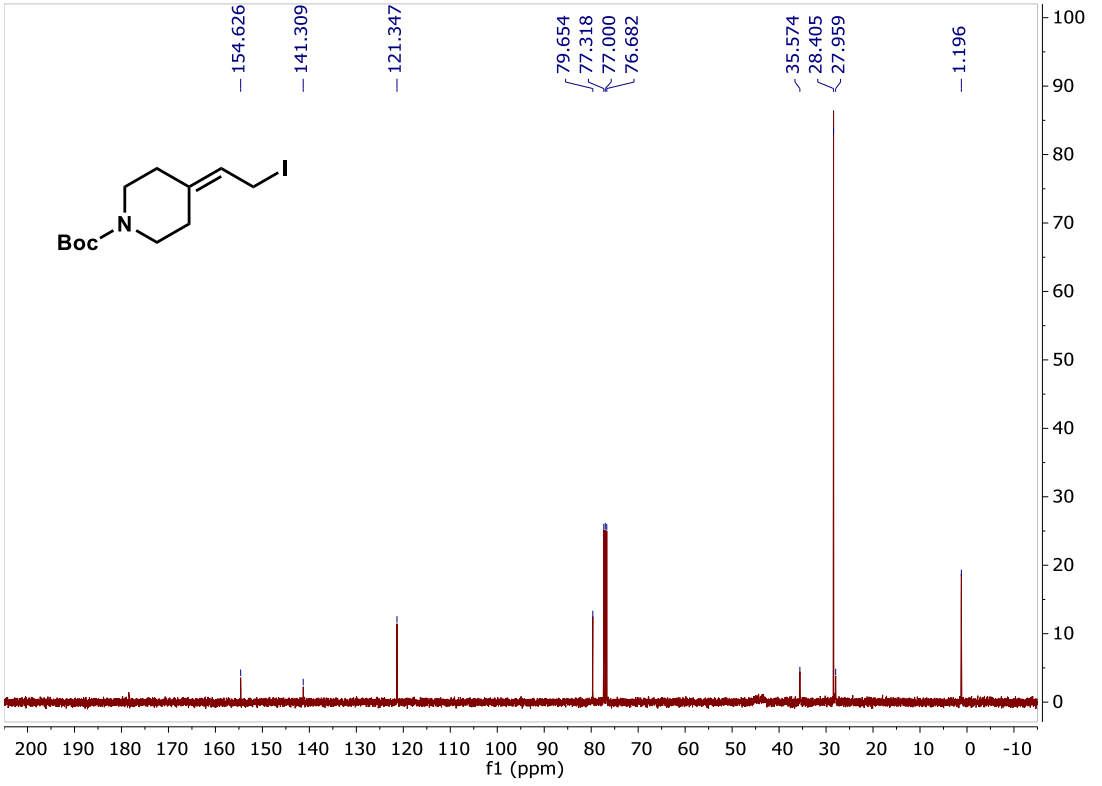
4-(2-Iodoethylidene)tetrahydro-2H-pyran, 1w



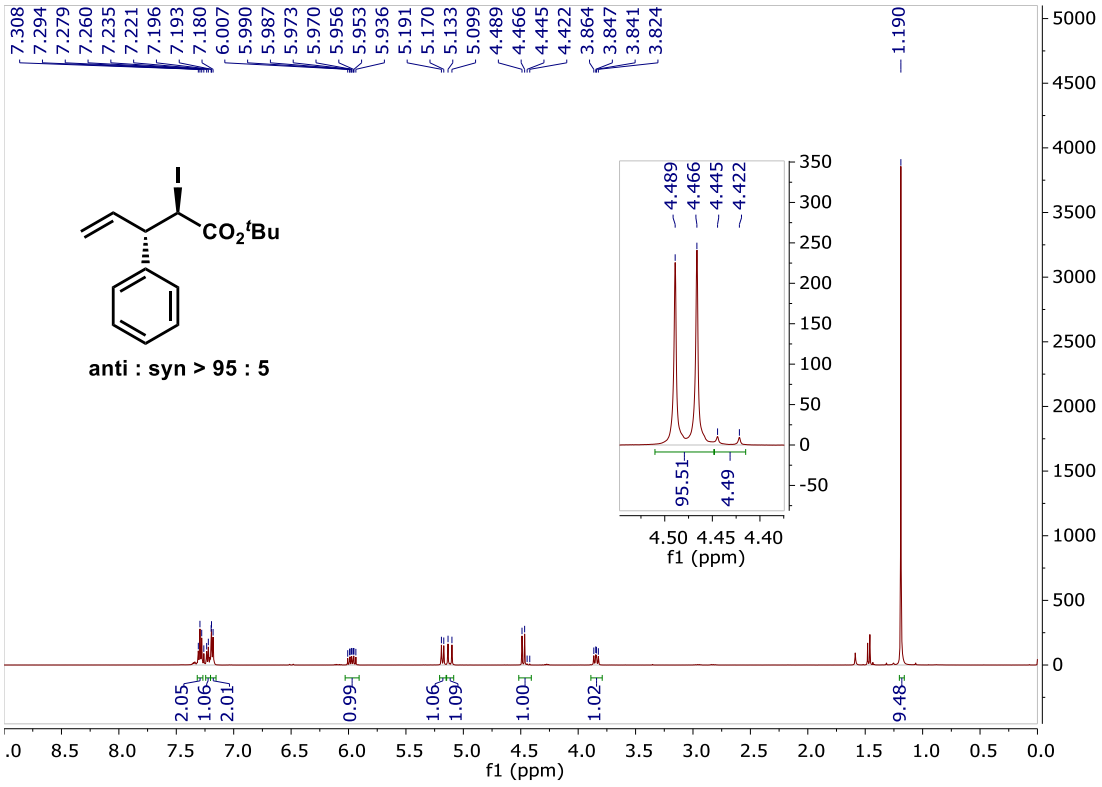


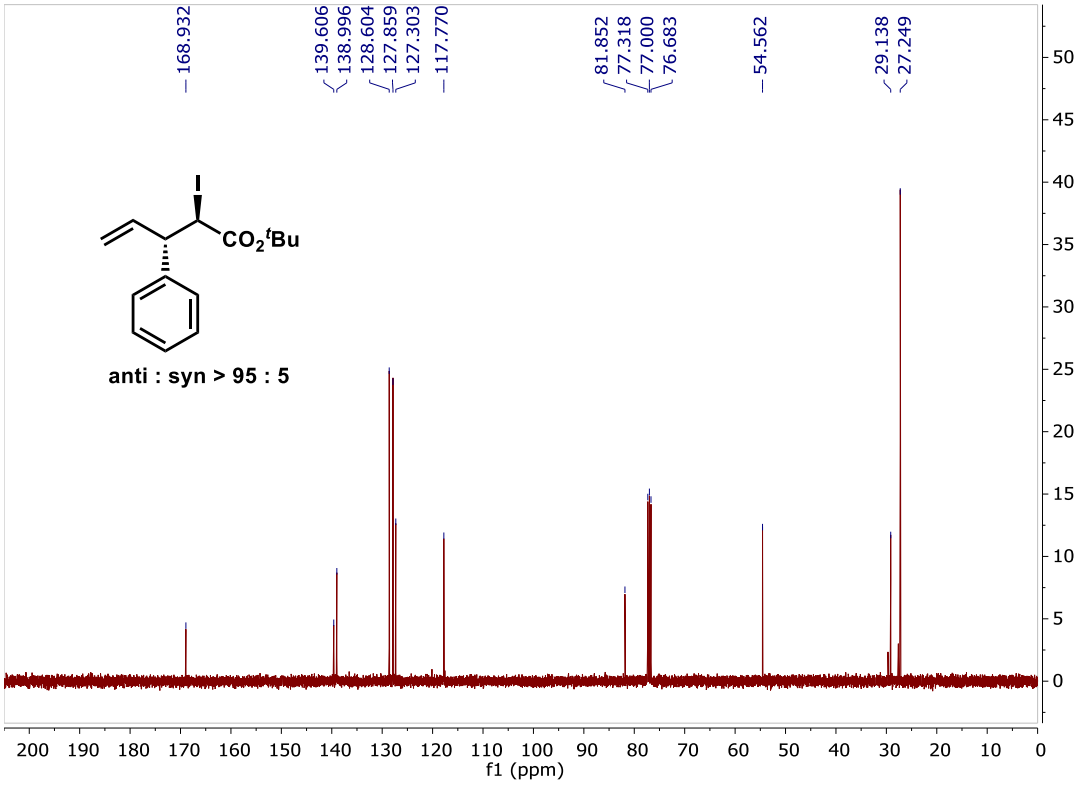
tert-Butyl 4-(2-iodoethylidene)piperidine-1-carboxylate, 1x



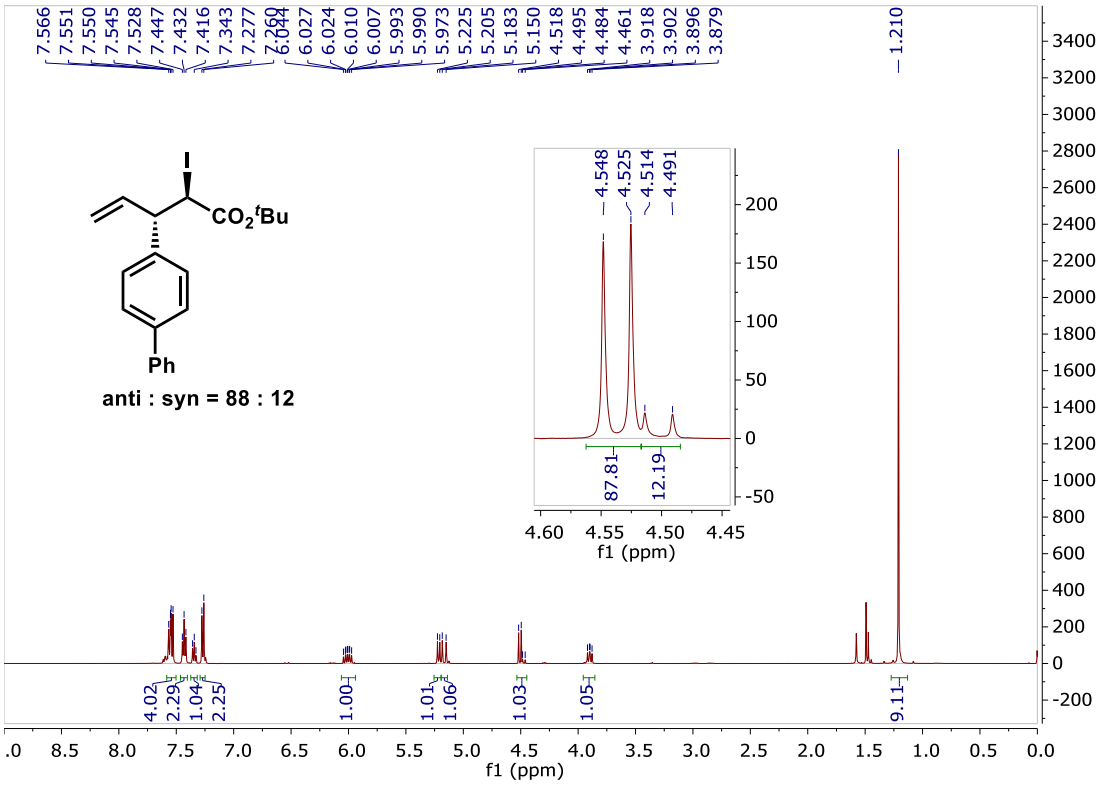


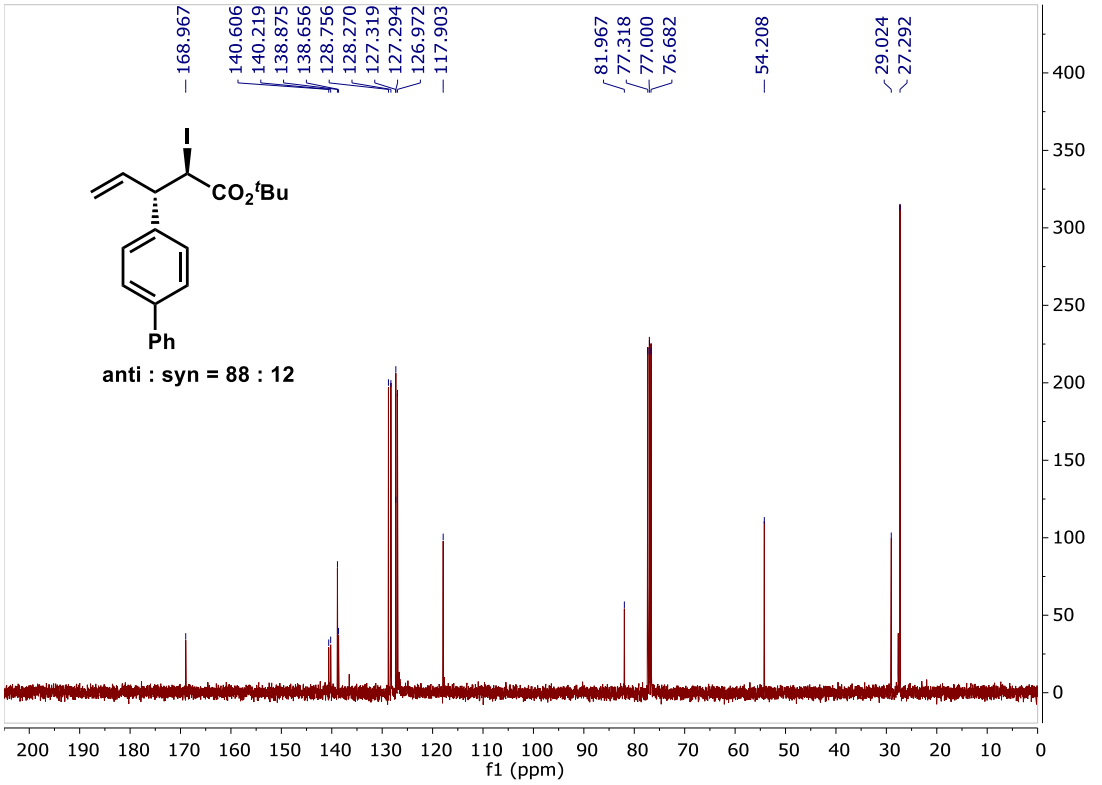
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-phenylpent-4-enoate, 5a



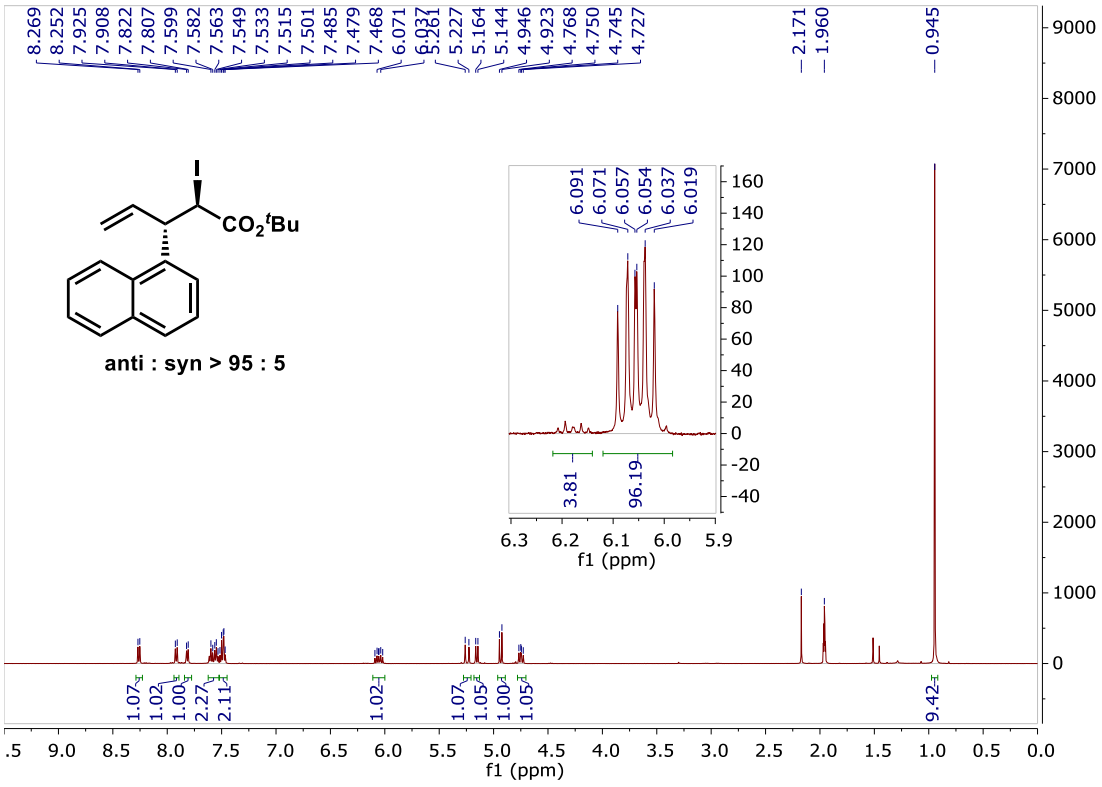


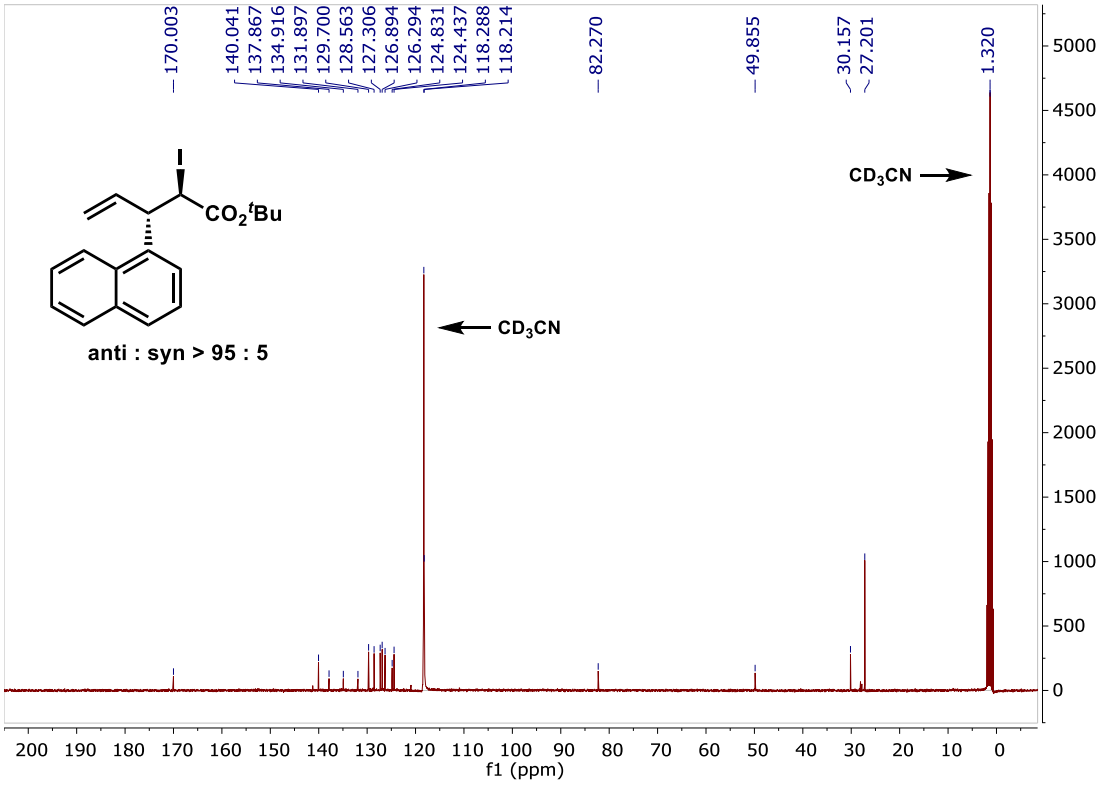
(+)-*tert*-Butyl (2*R*, 3*S*)-3-([1,1'-biphenyl]-4-yl)-2-iodopent-4-enoate, 5b



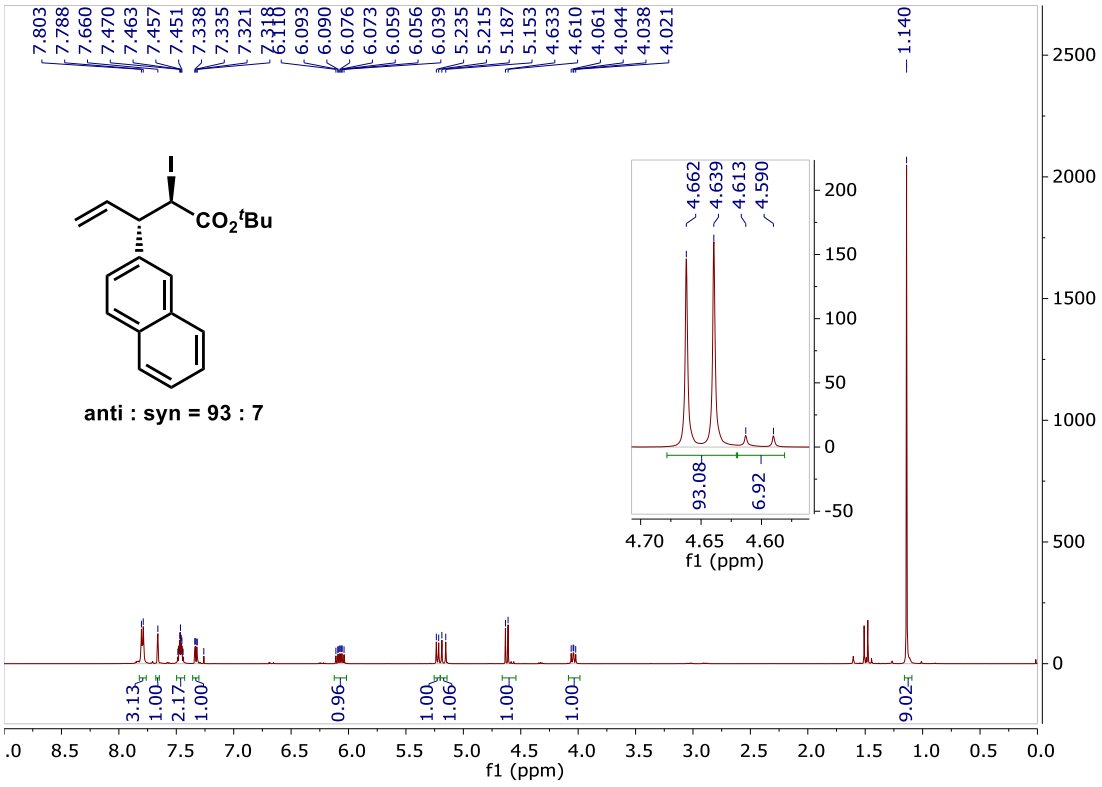


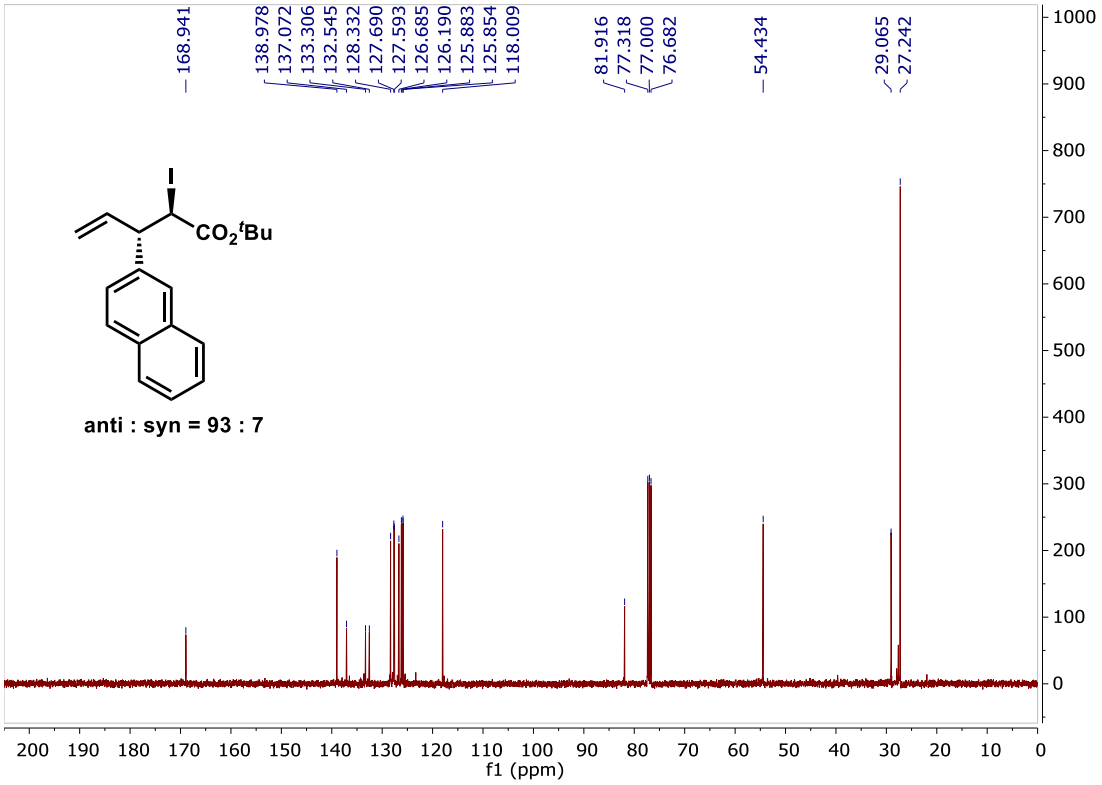
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(naphthalen-1-yl)pent-4-enoate, 5c



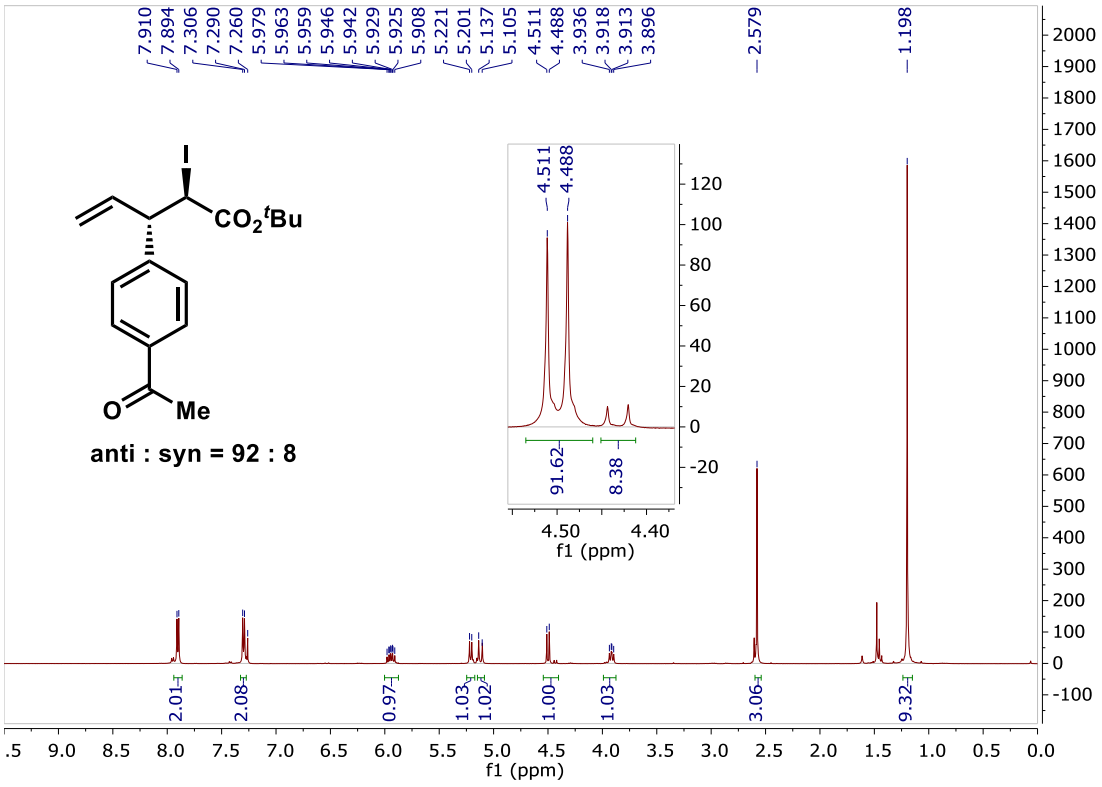


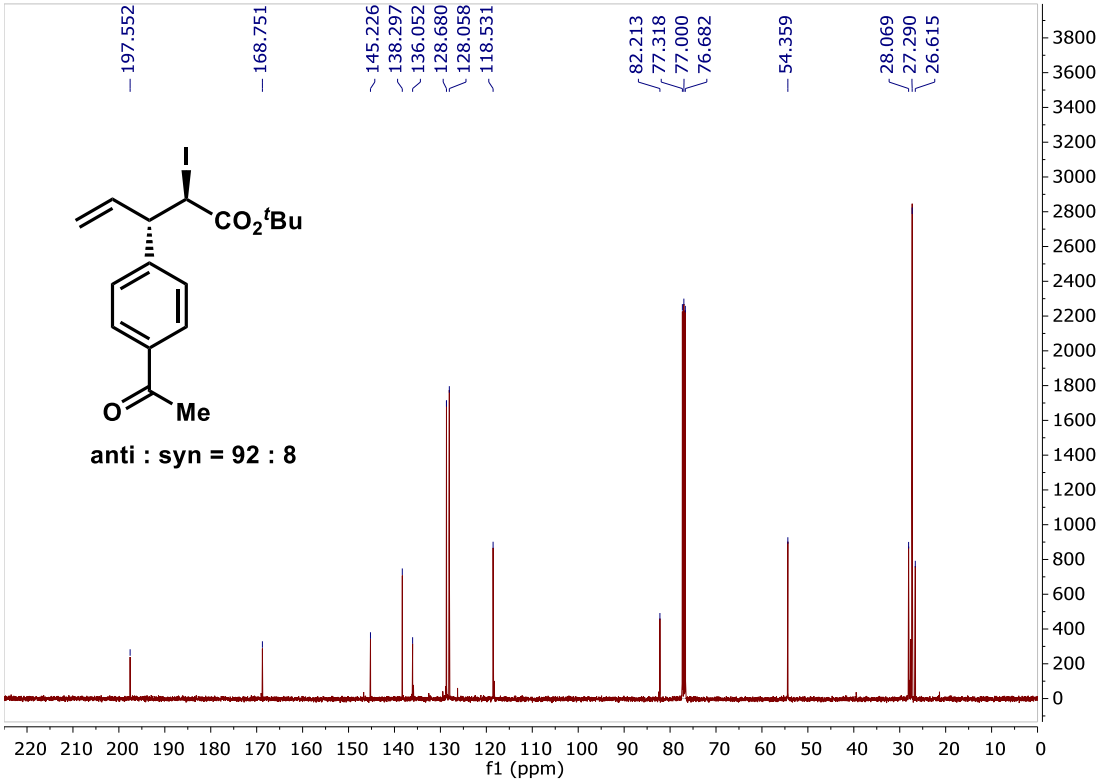
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(naphthalen-2-yl)pent-4-enoate, 5d



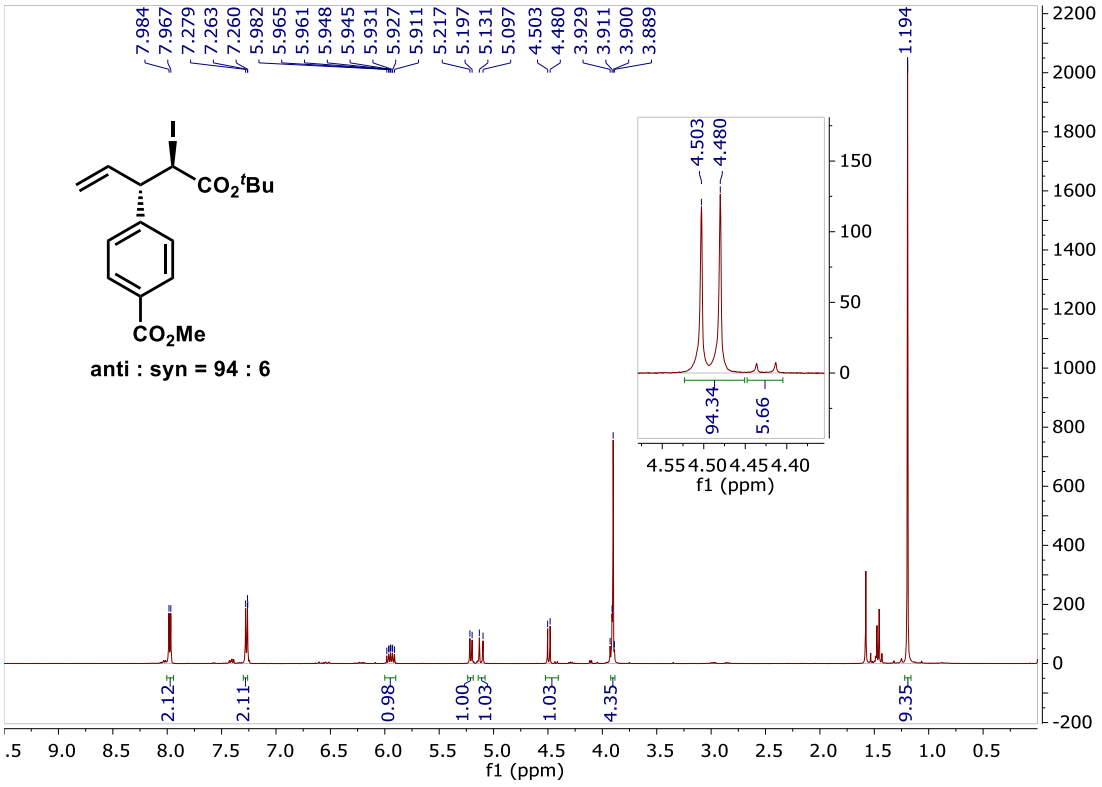


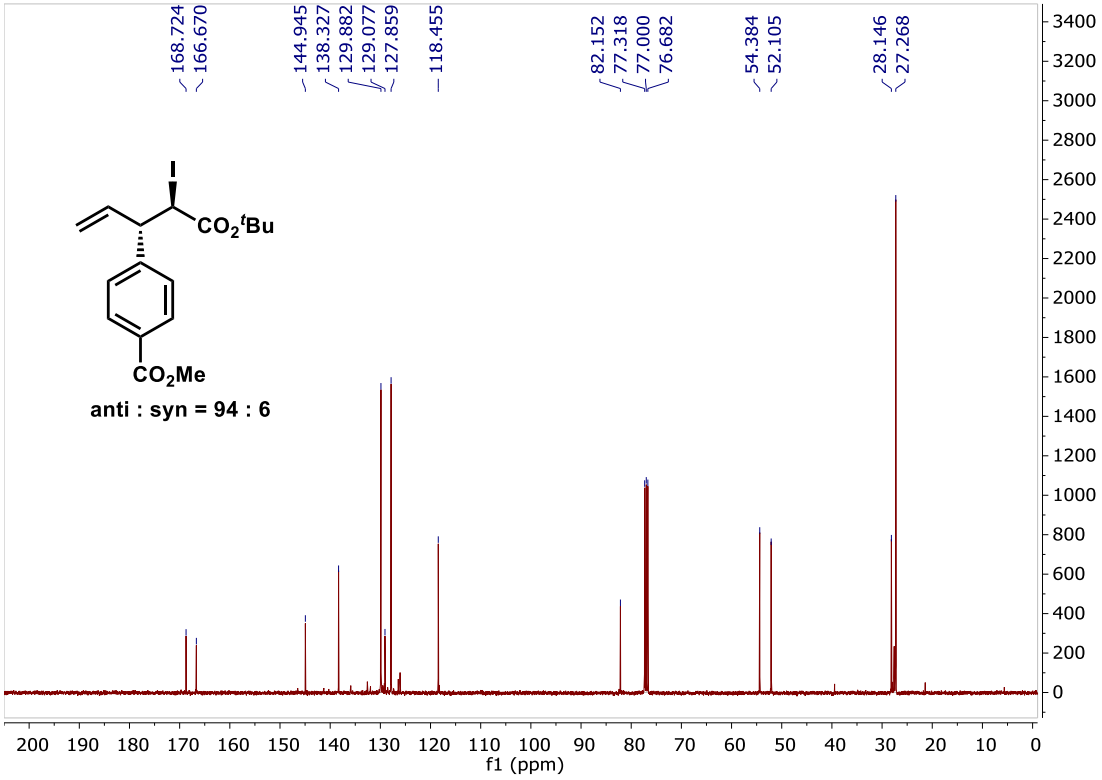
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-acetylphenyl)-2-iodopent-4-enoate, 5e



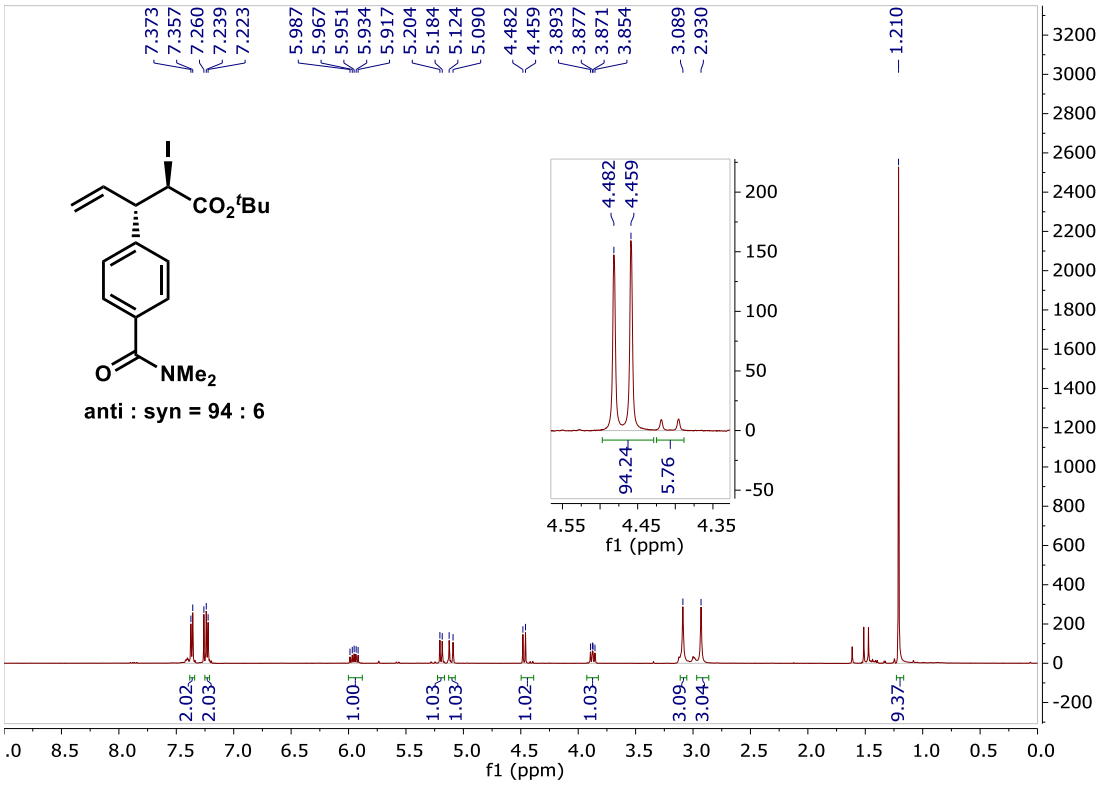


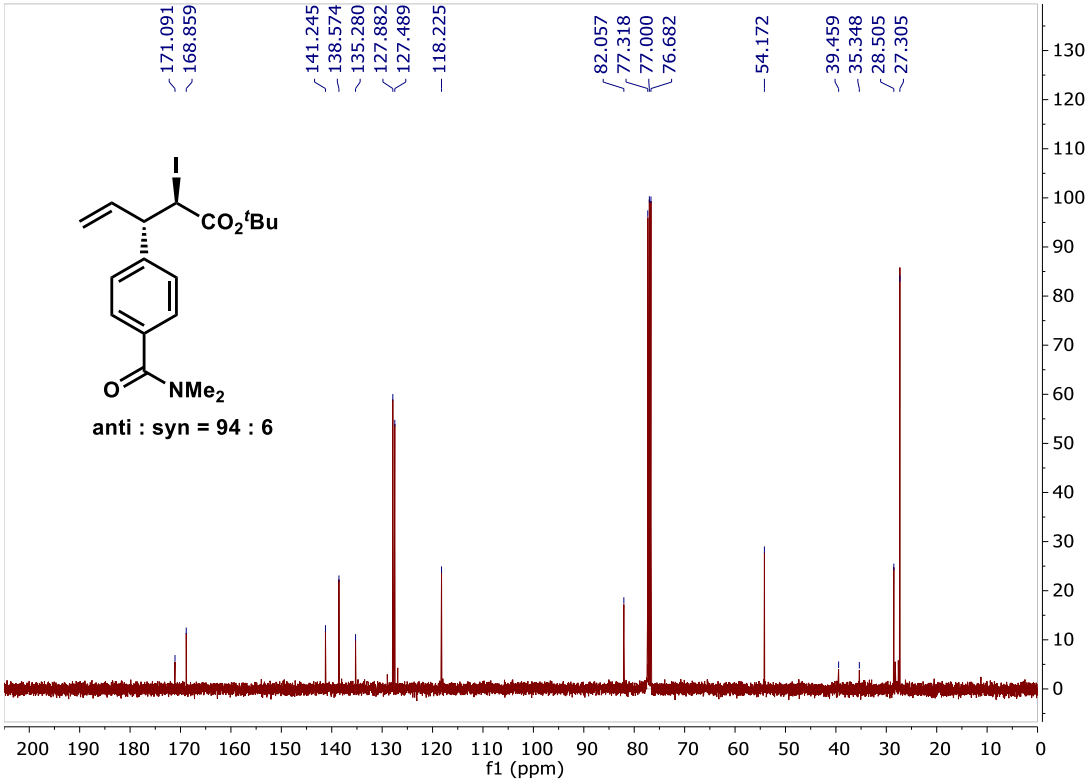
(+)-Methyl 4-((3*S*, 4*R*)-5-(*tert*-butoxy)-4-iodo-5-oxopent-1-en-3-yl)benzoate, 5f



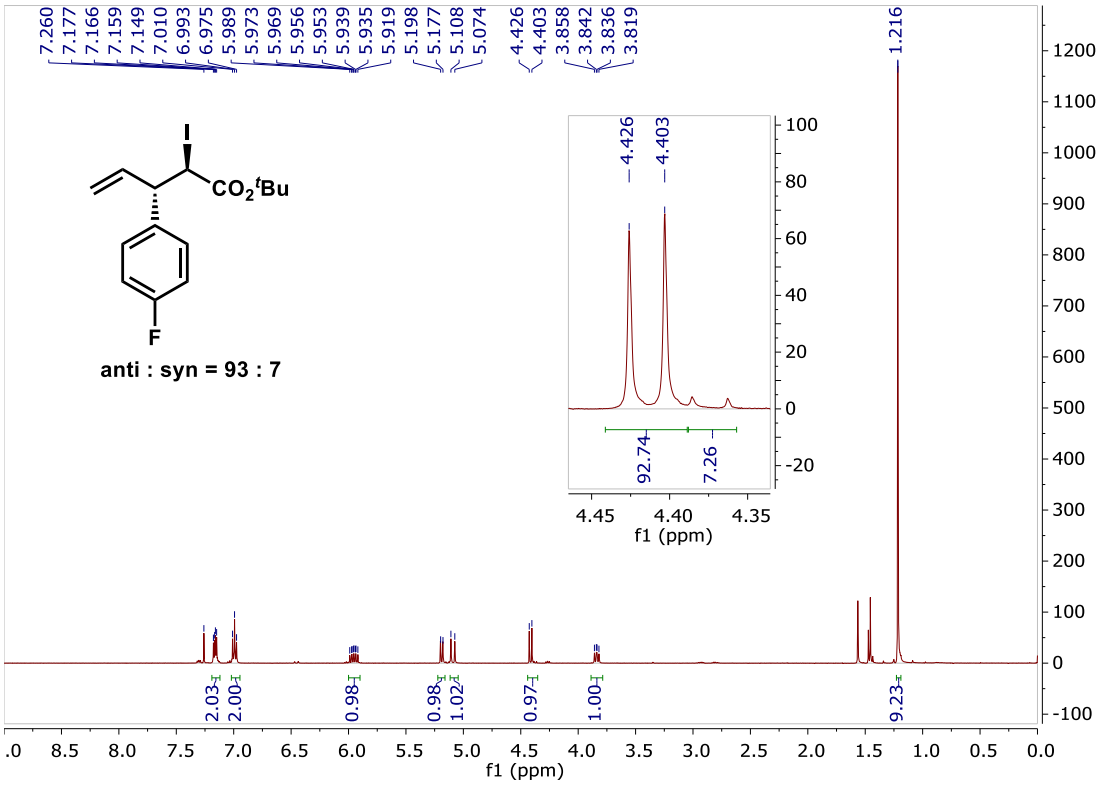


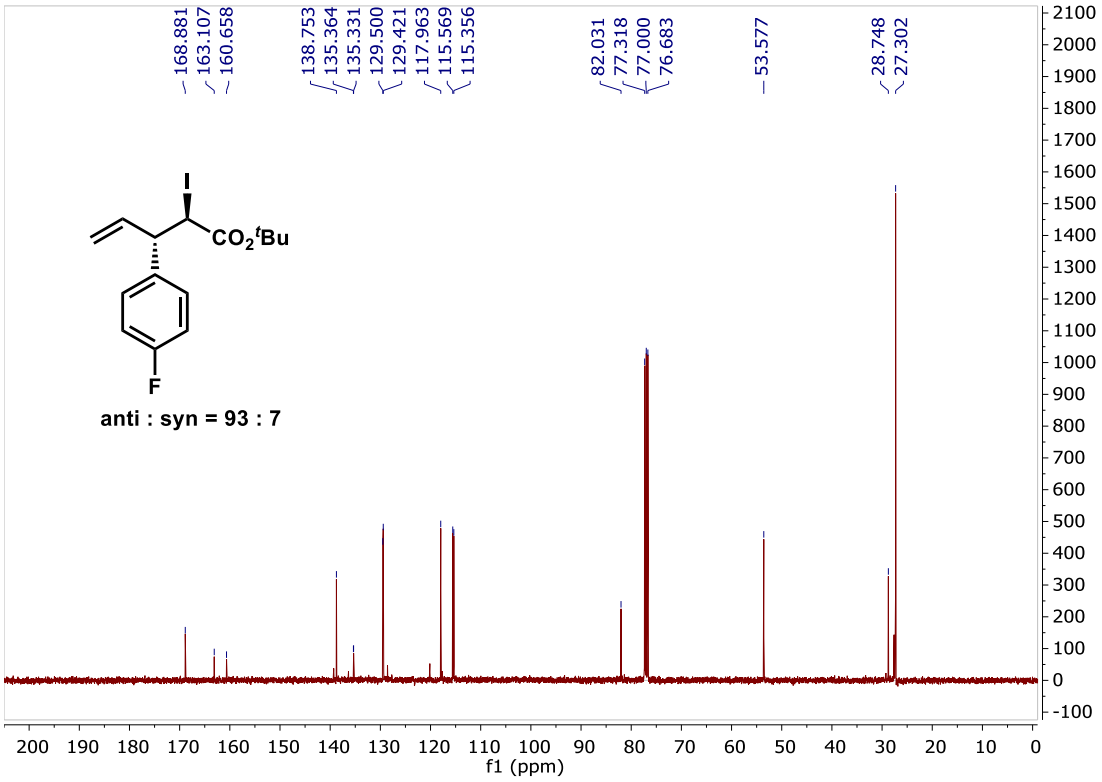
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-(dimethylcarbamoyl)phenyl)-2-iodopent-4-enoate, 5g



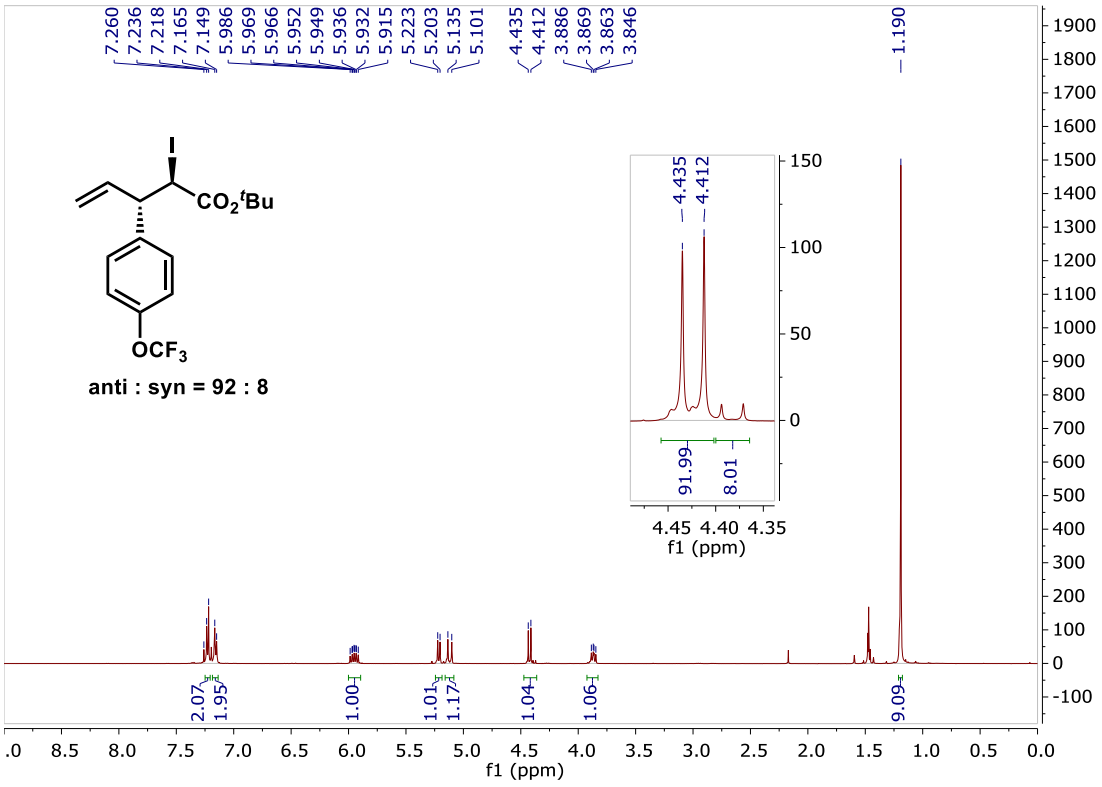


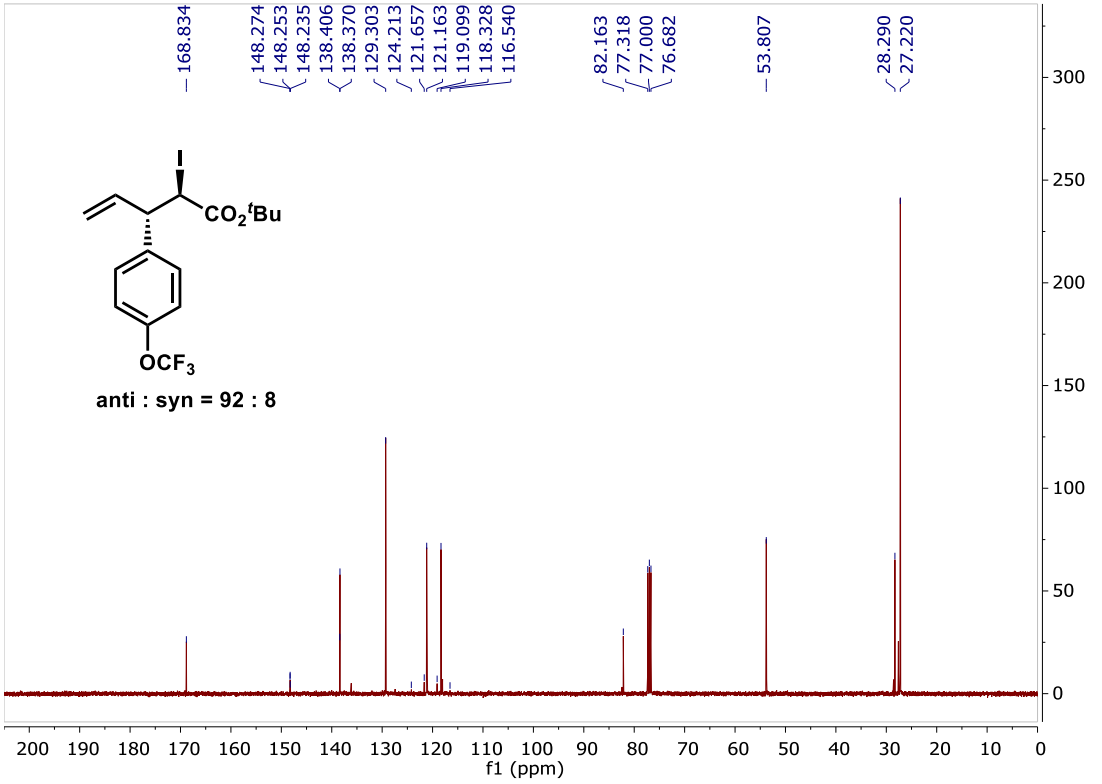
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-fluorophenyl)-2-iodopent-4-enoate, 5h



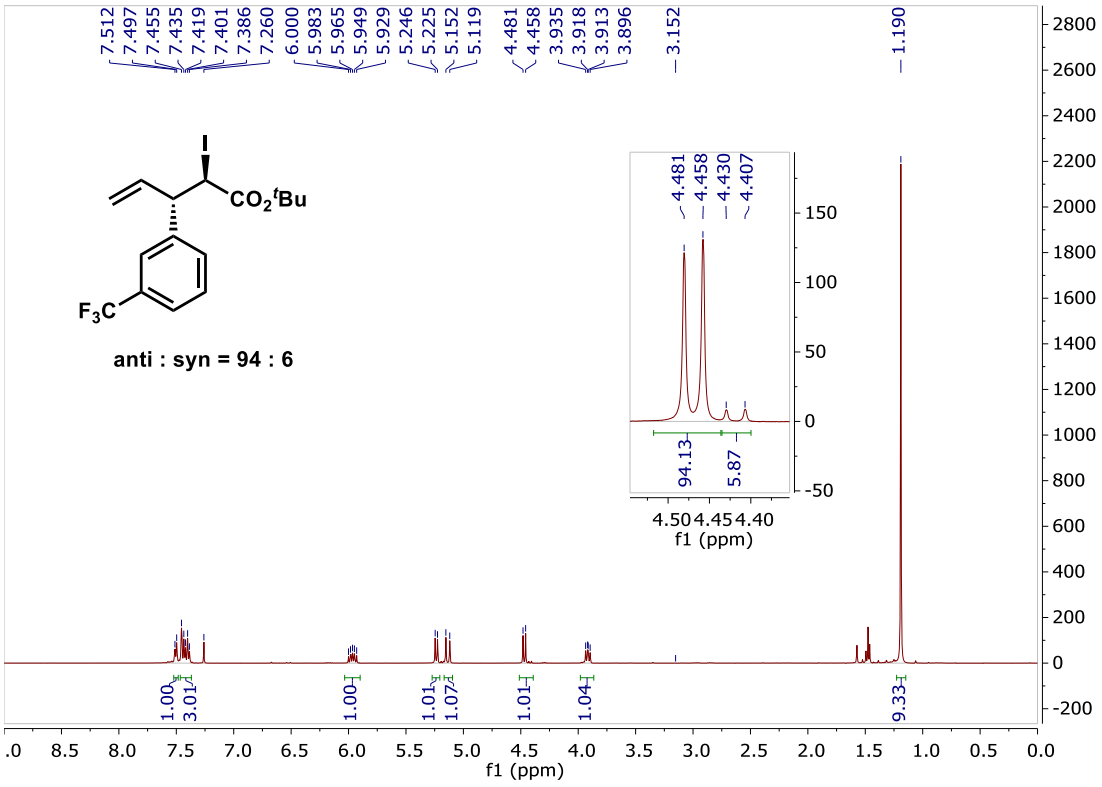


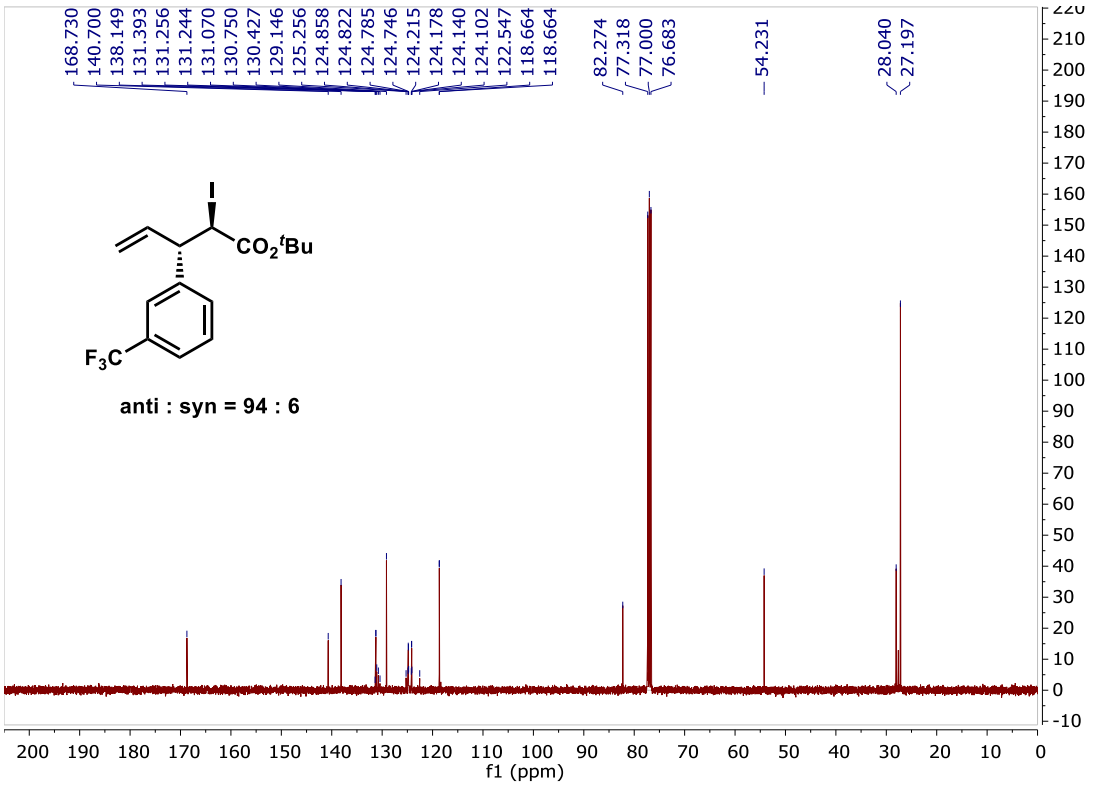
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(4-(trifluoromethoxy)phenyl)pent-4-enoate, 5i



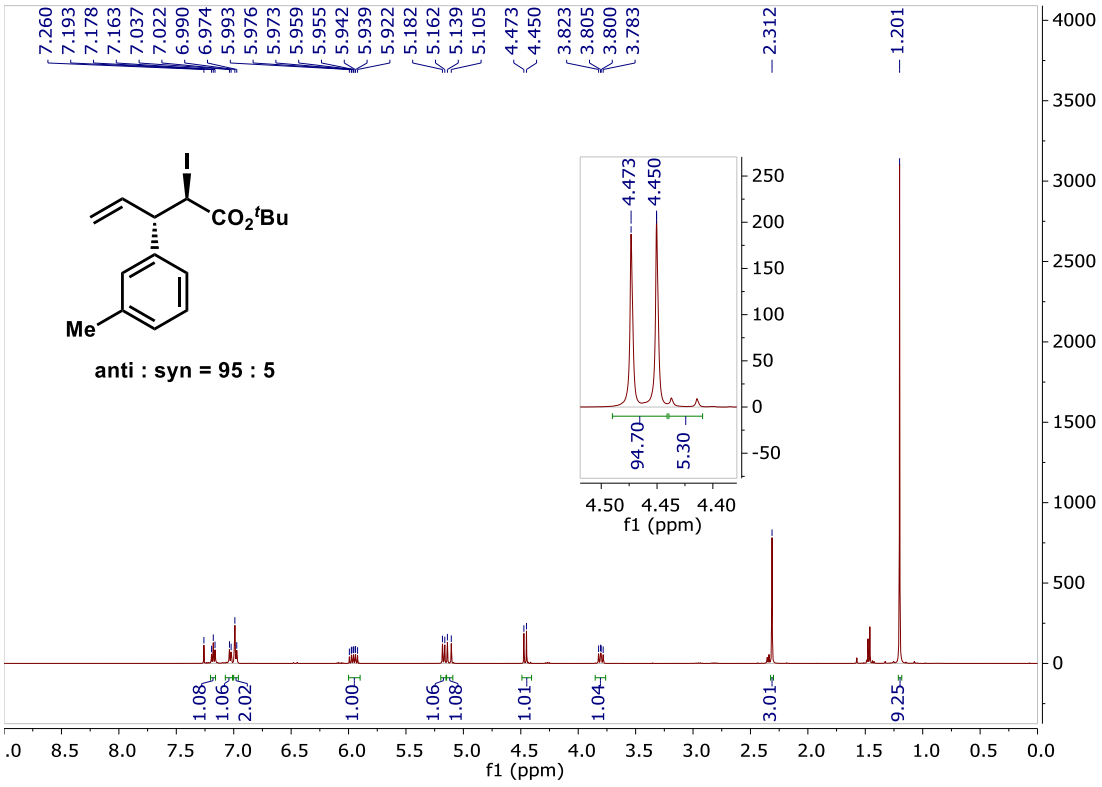


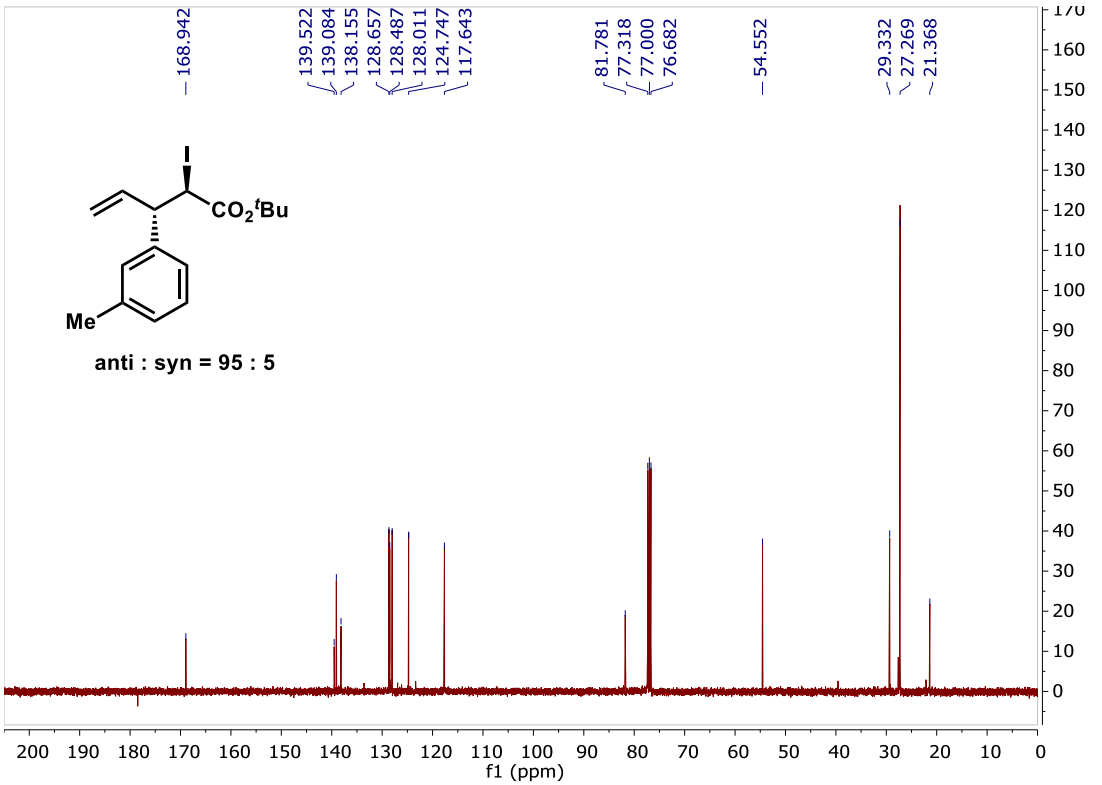
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(3-(trifluoromethyl)phenyl)pent-4-enoate, 5j



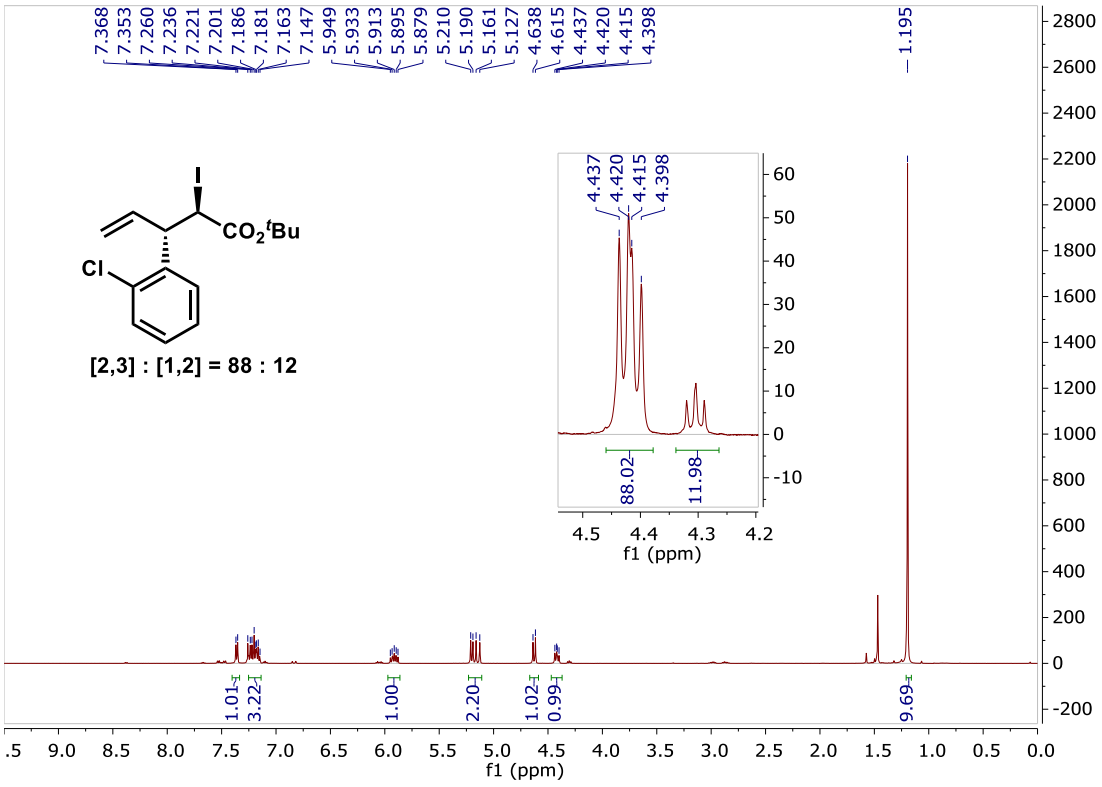


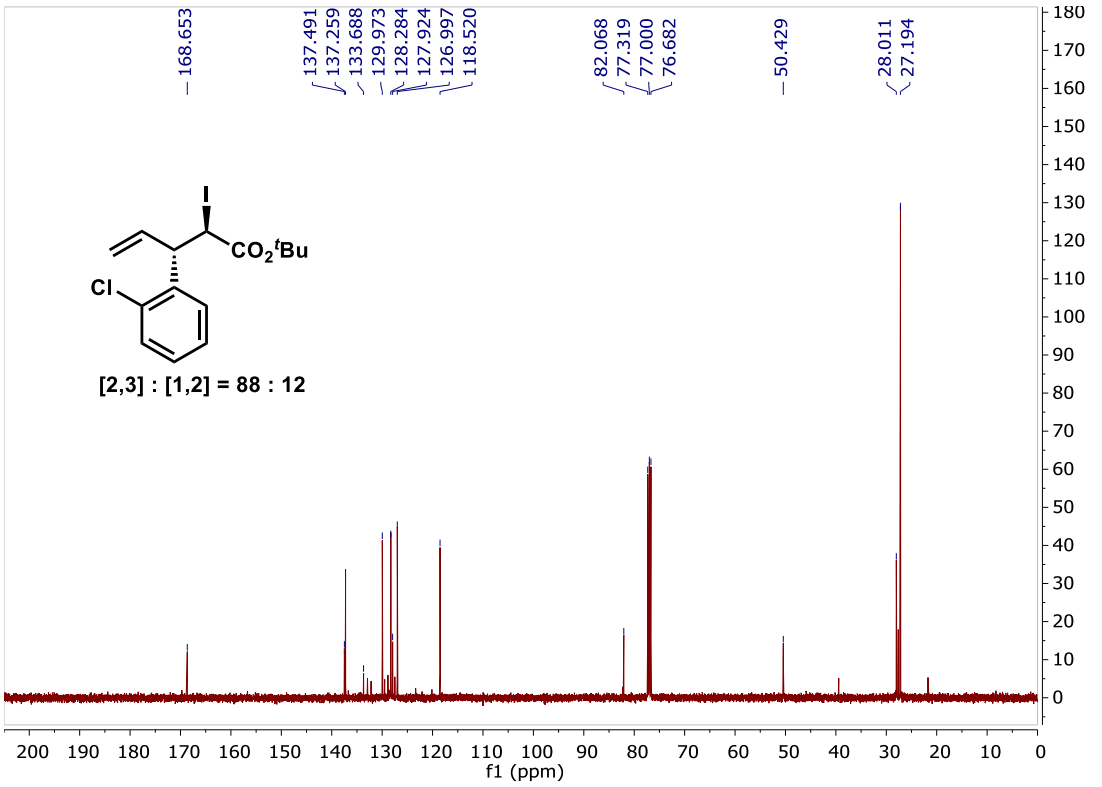
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(*m*-tolyl)pent-4-enoate, 5k



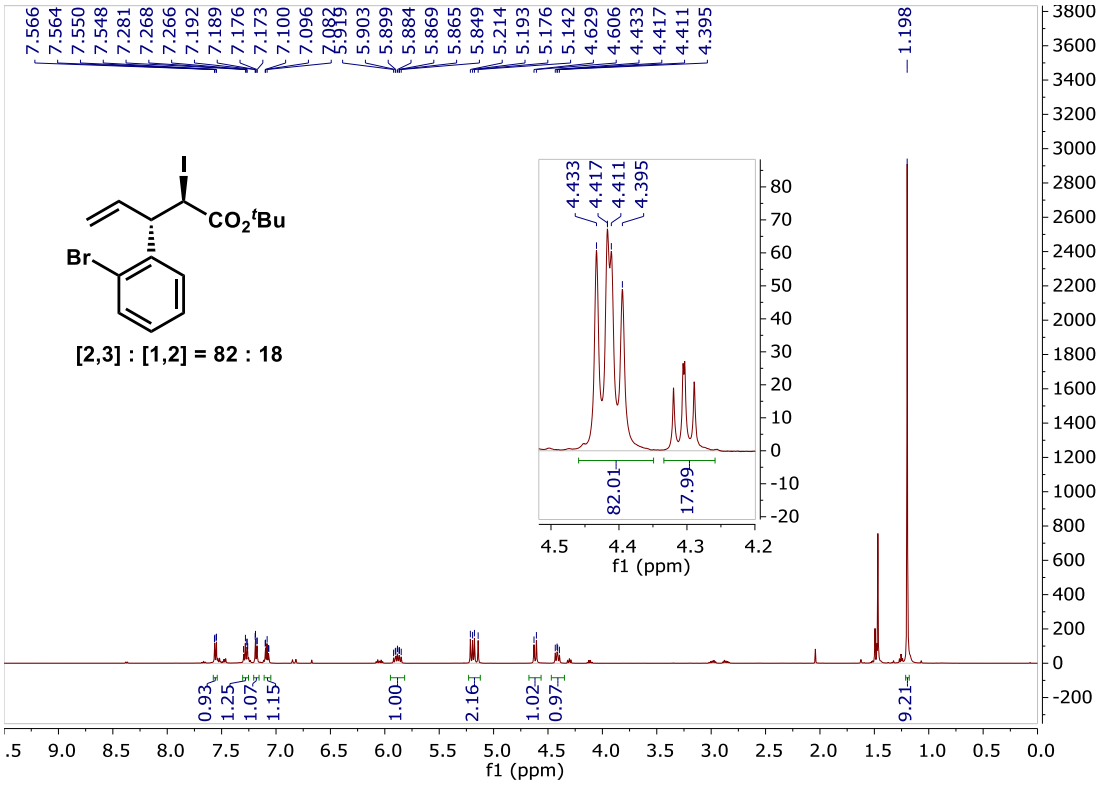


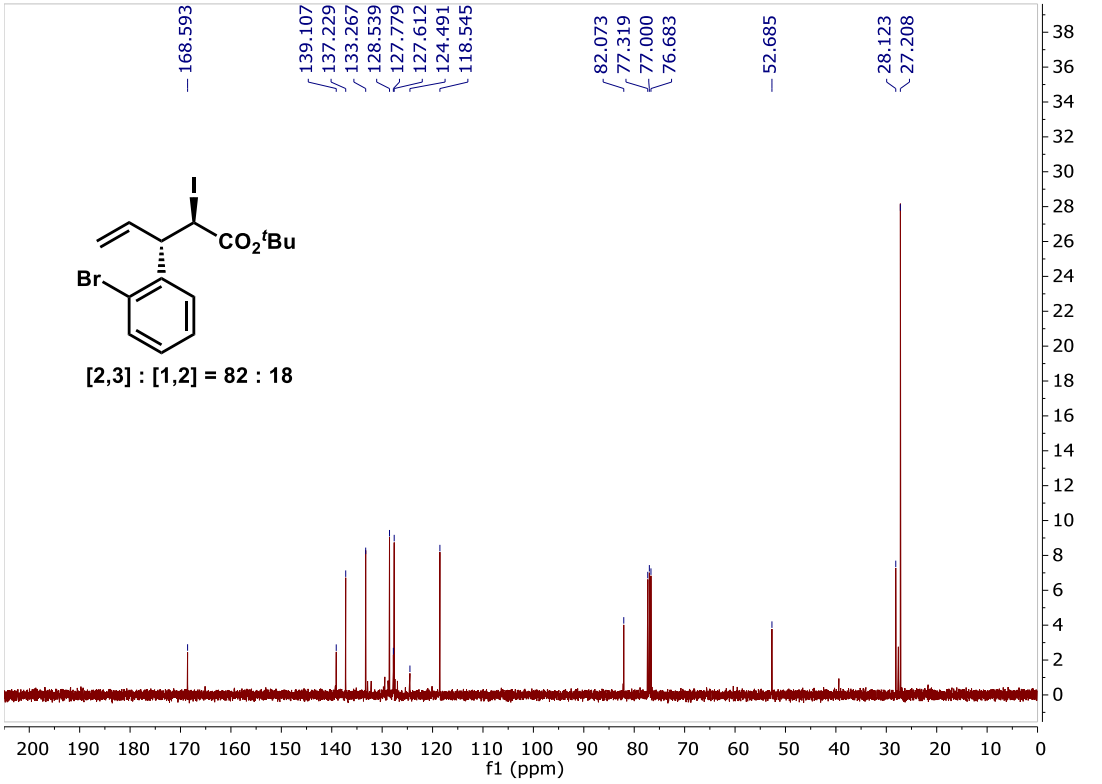
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-chlorophenyl)-2-iodopent-4-enoate, 5l



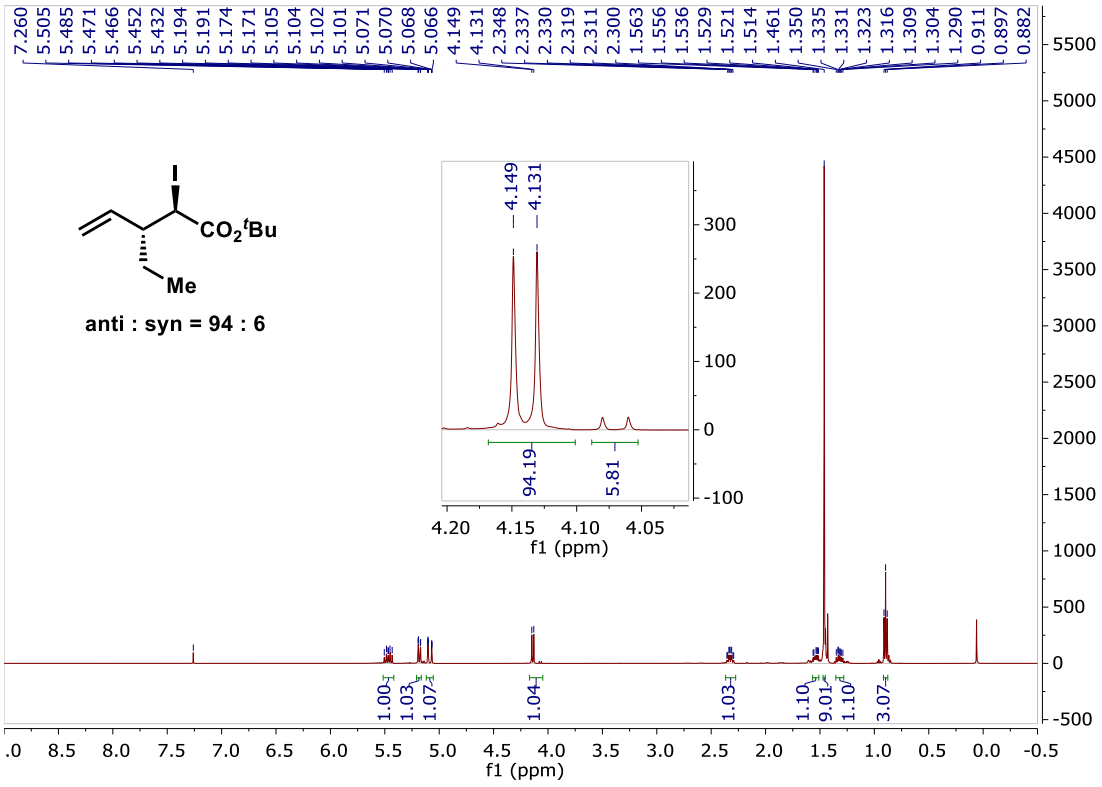


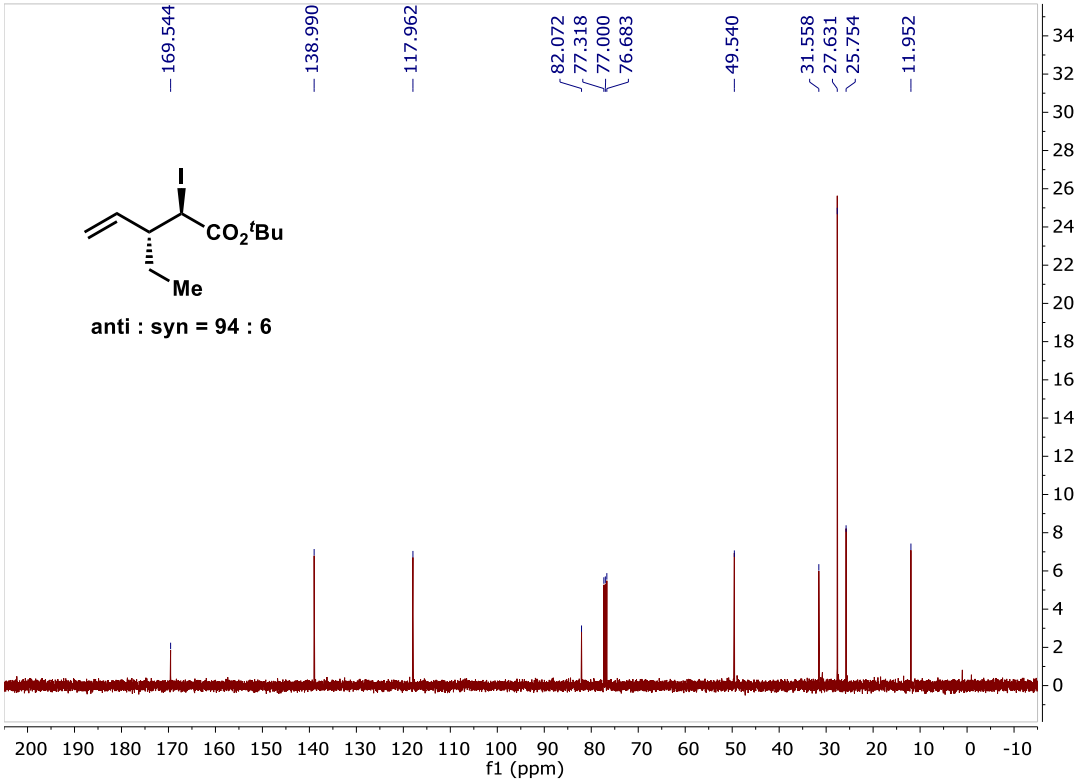
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-bromophenyl)-2-iodopent-4-enoate, 5m



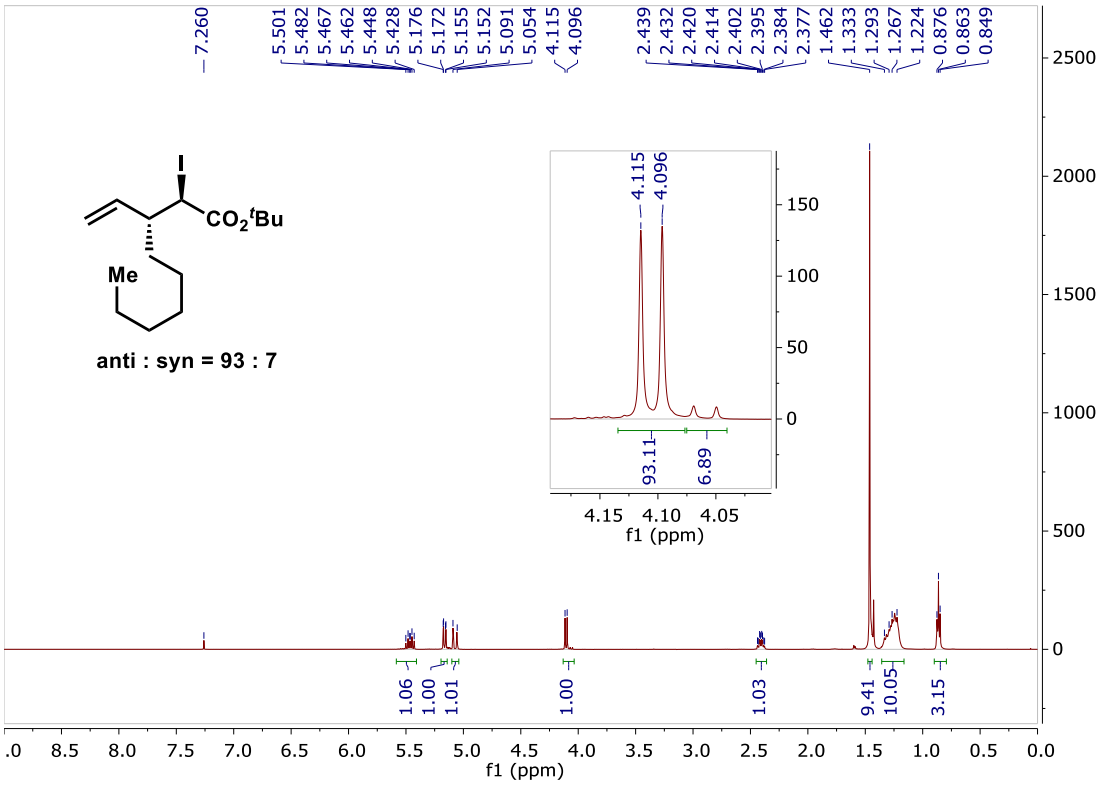


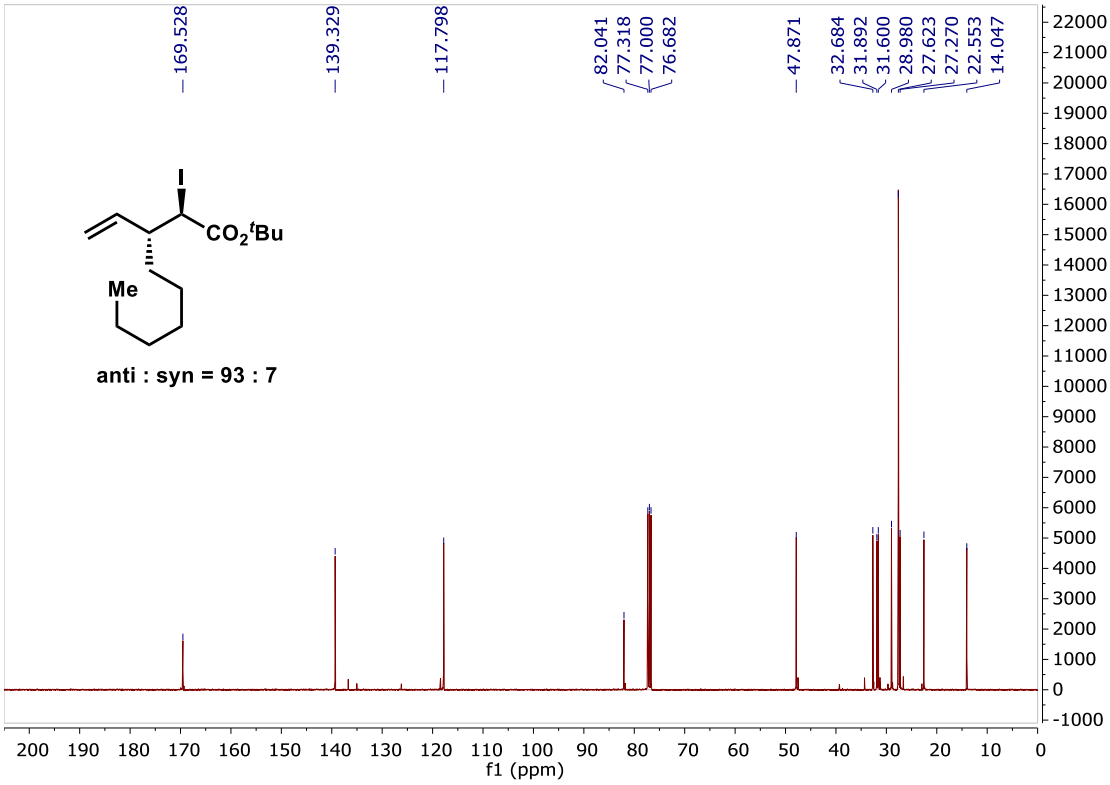
(+)-*tert*-Butyl (2*R*, 3*R*)-3-ethyl-2-iodopent-4-enoate, 5n



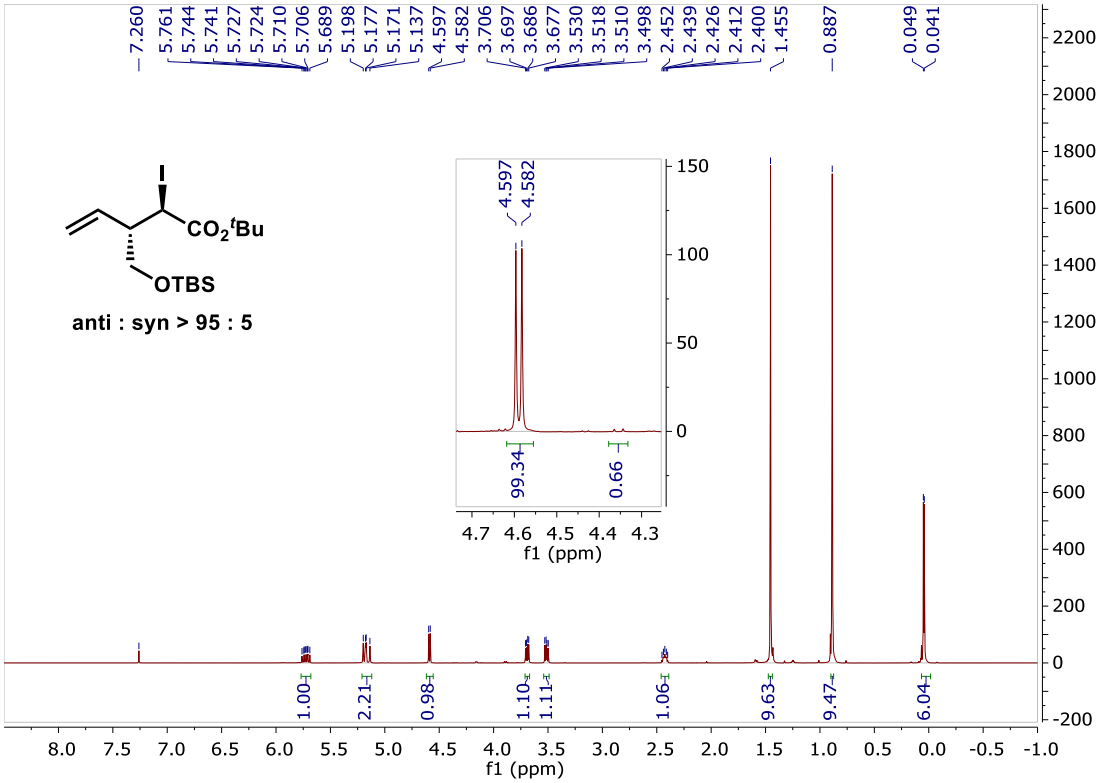


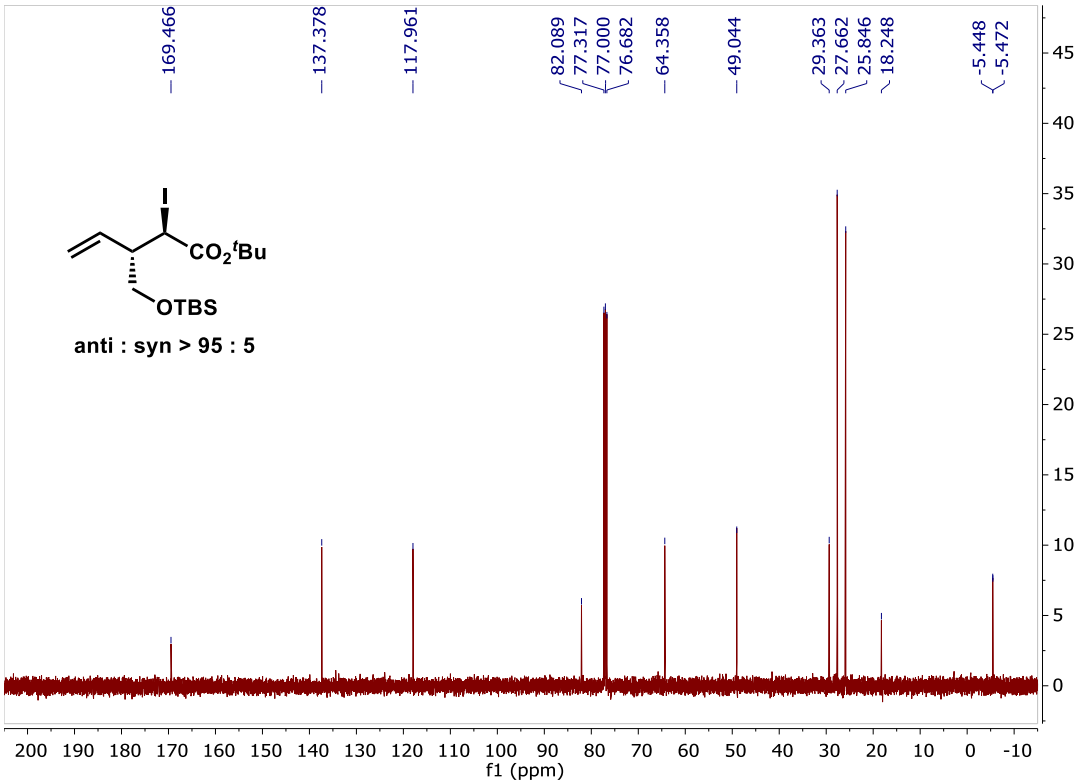
(+)-*tert*-Butyl (2*R*, 3*R*)-2-iodo-3-vinylnonanoate, 5o



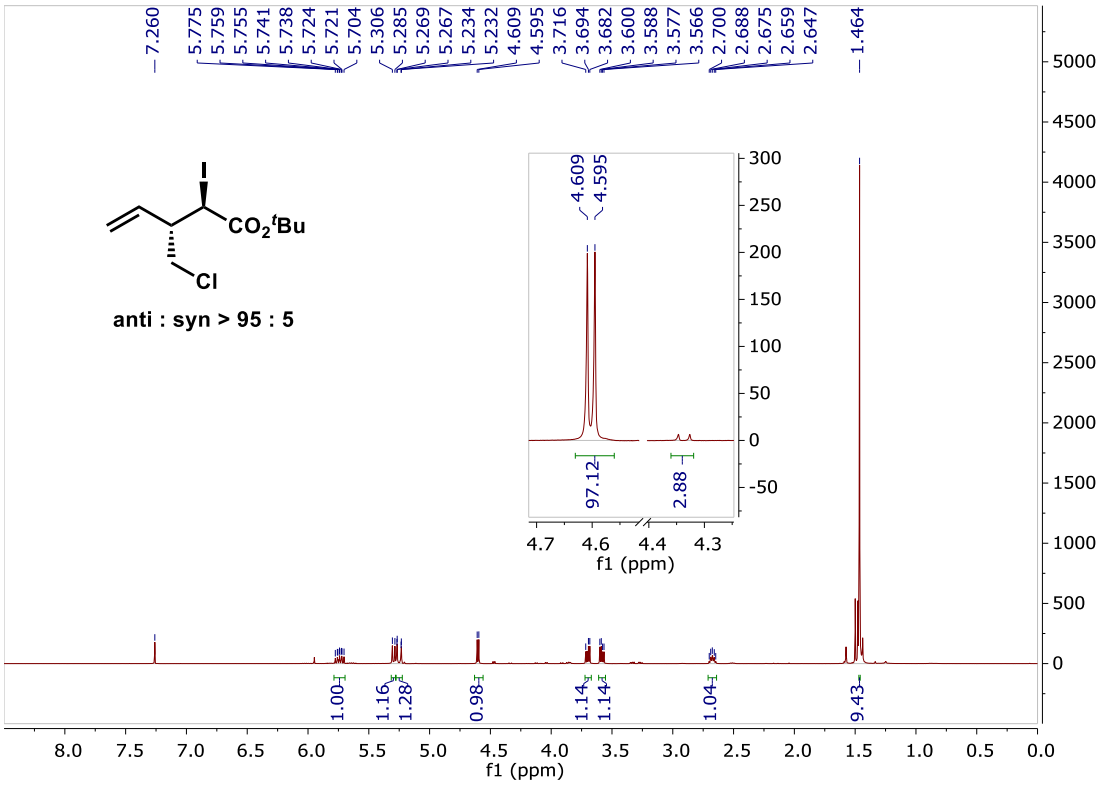


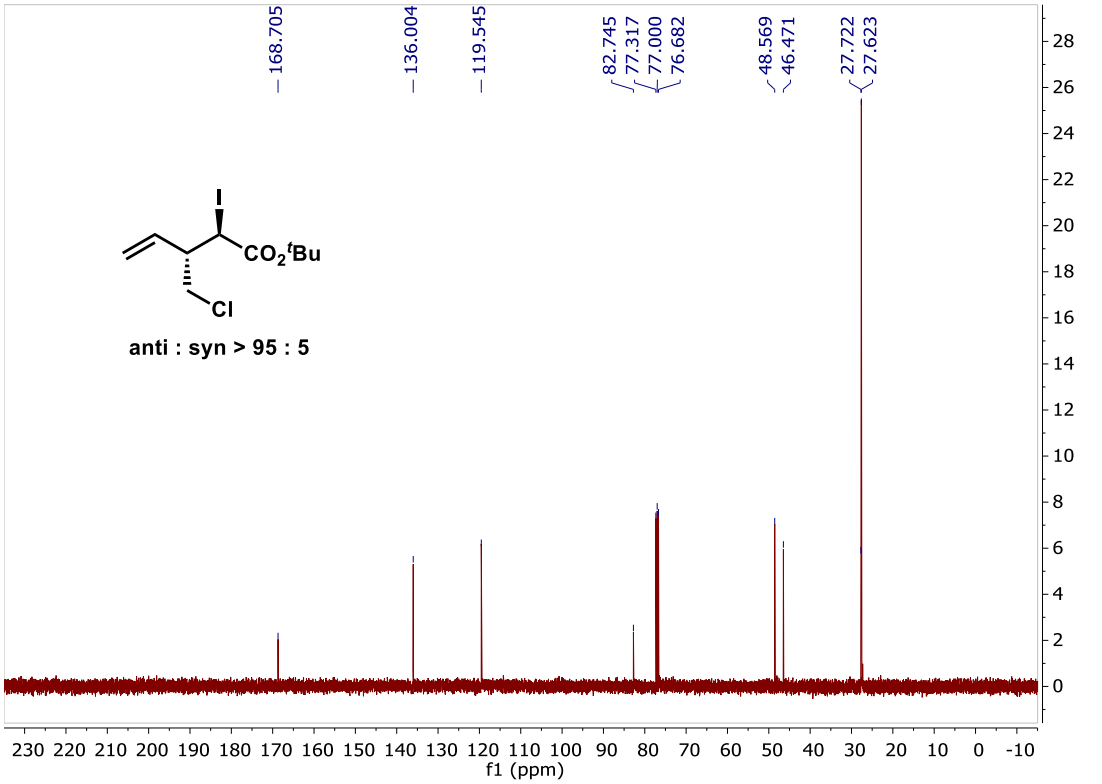
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-iodopent-4-enoate, 5p



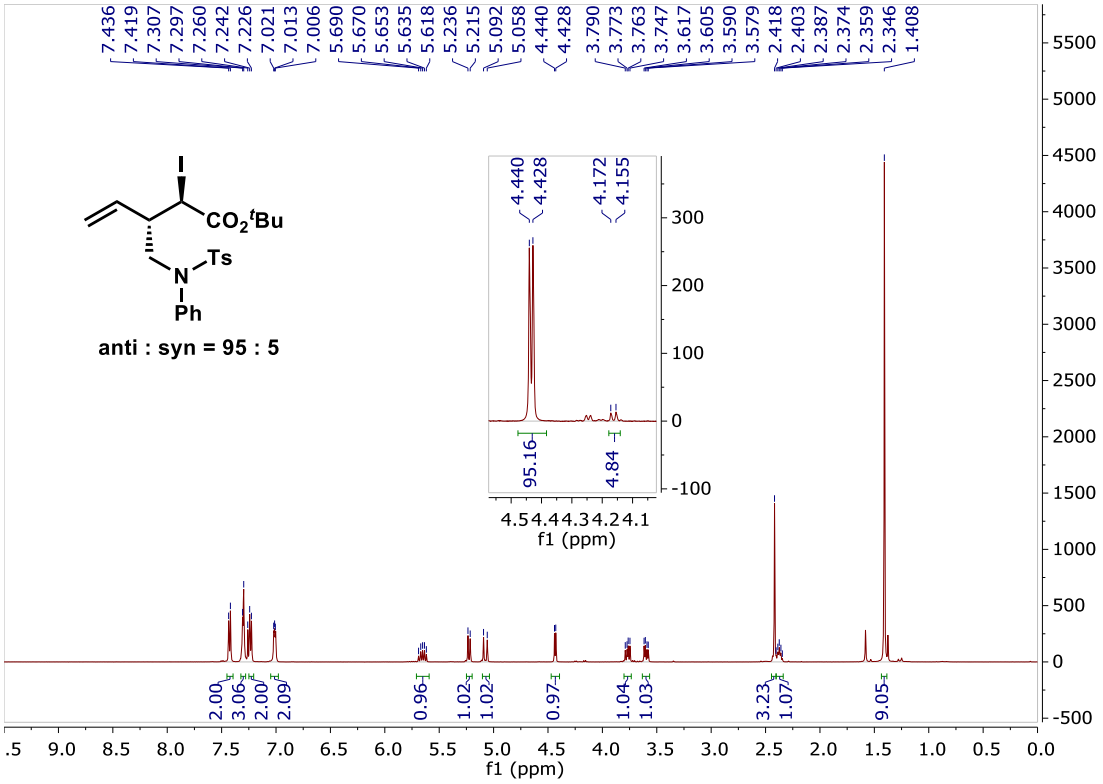


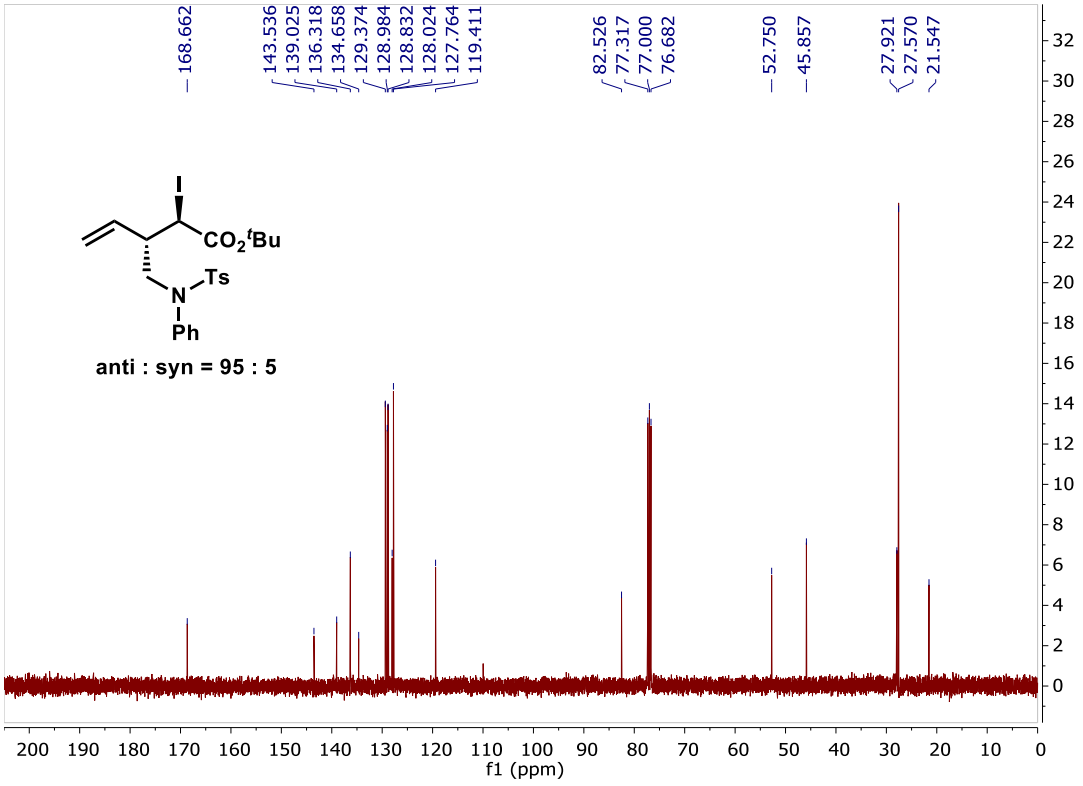
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(chloromethyl)-2-iodopent-4-enoate, 5q



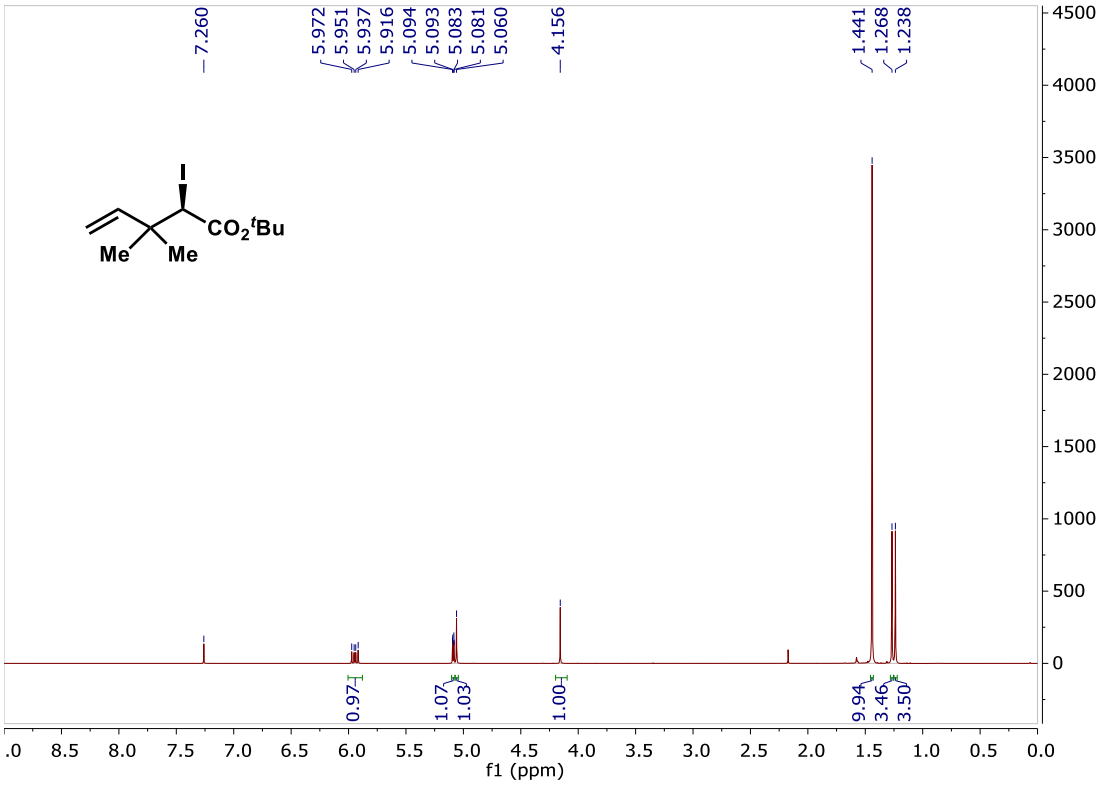


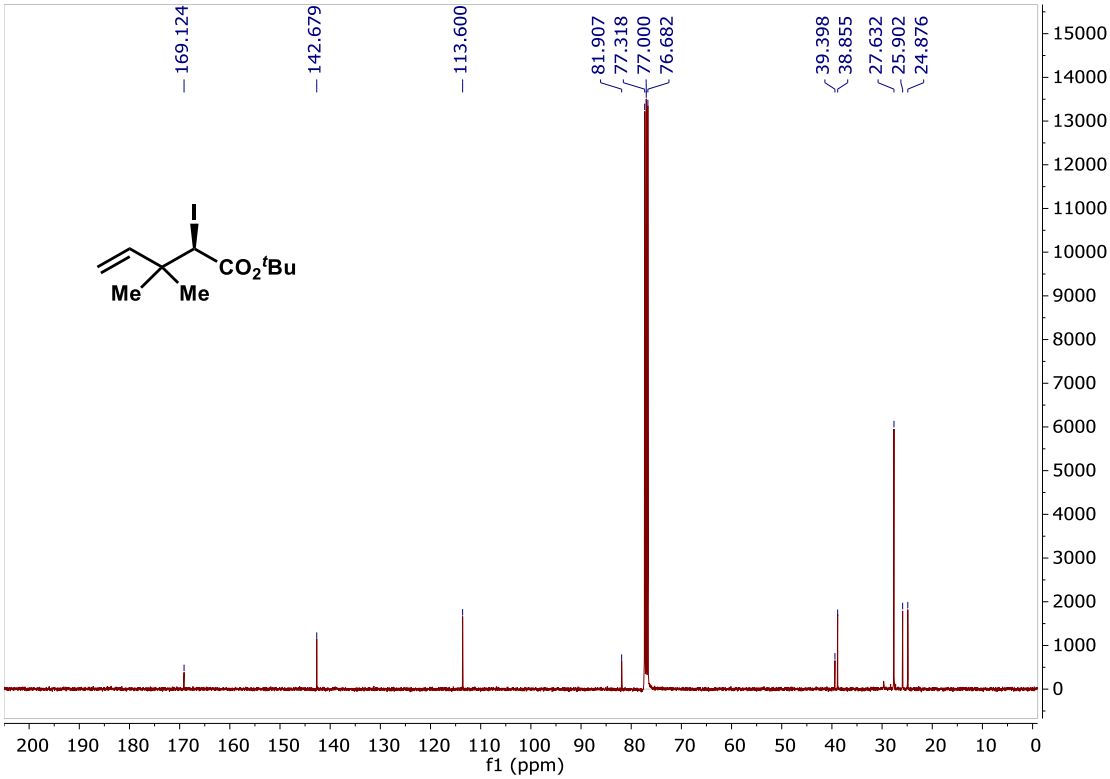
(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(((4-methyl-*N*-phenylphenyl)sulfonamido)methyl)pent-4-enoate, 5r



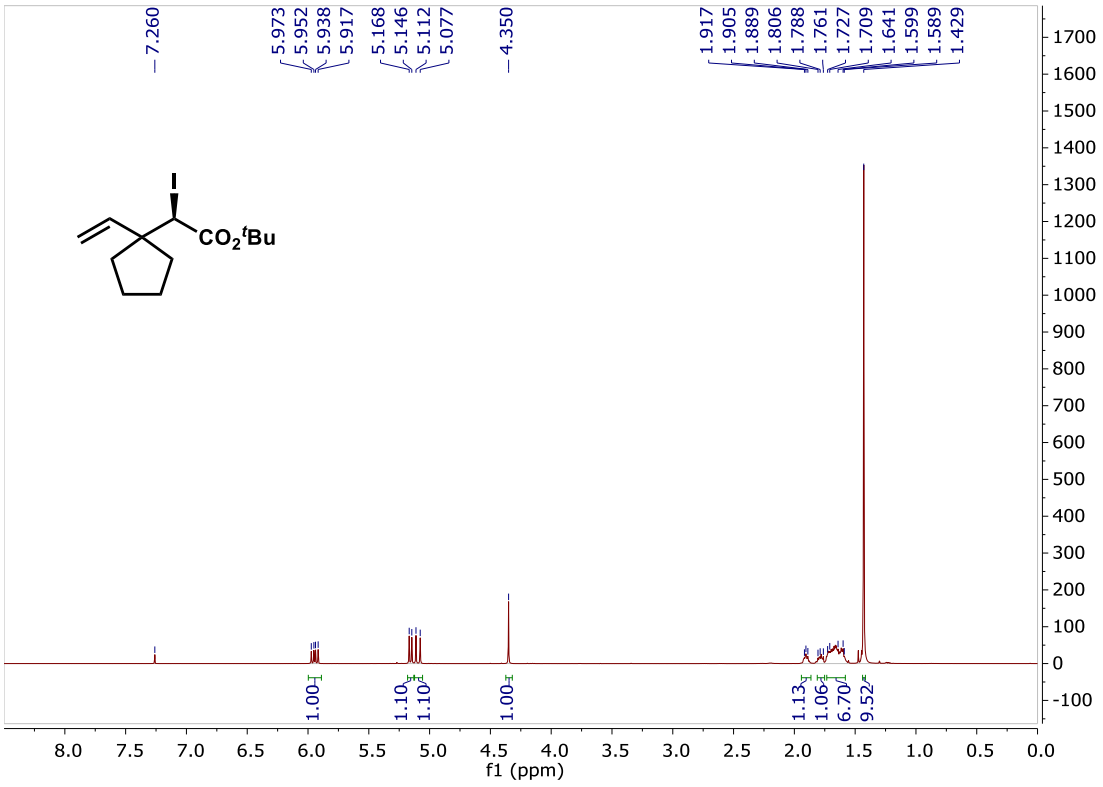


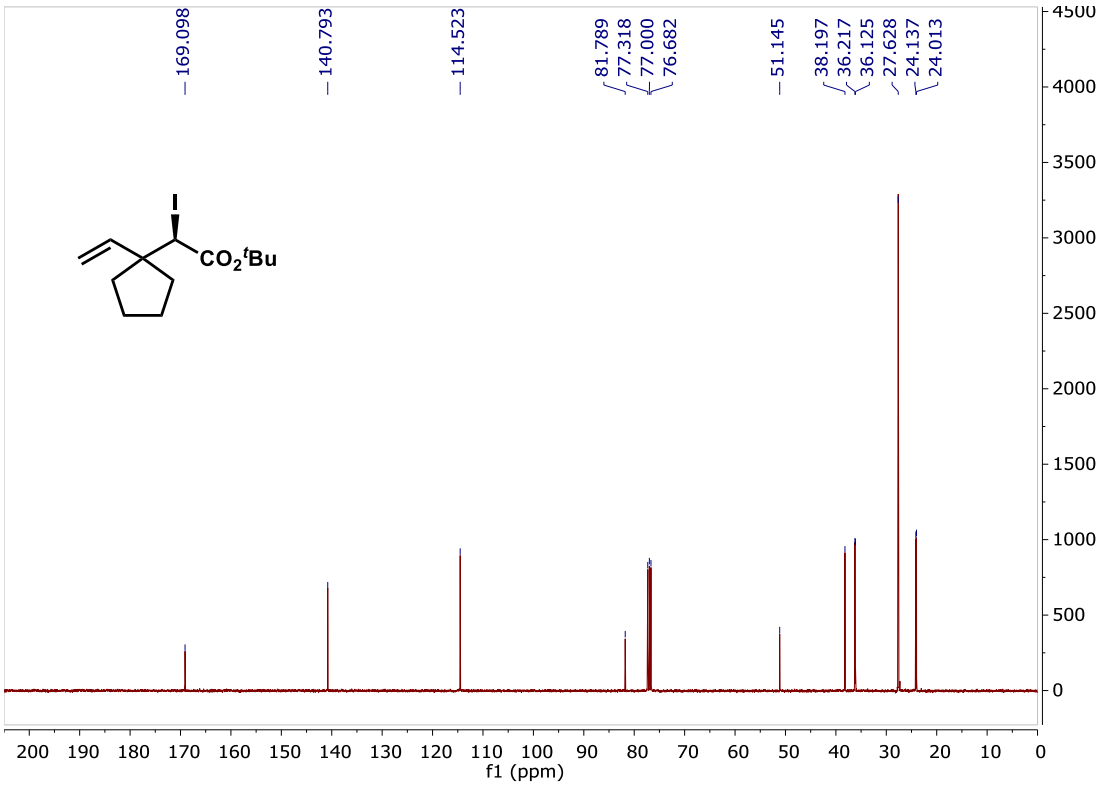
(+)-*tert*-Butyl (*R*)-2-iodo-3,3-dimethylpent-4-enoate, 5s



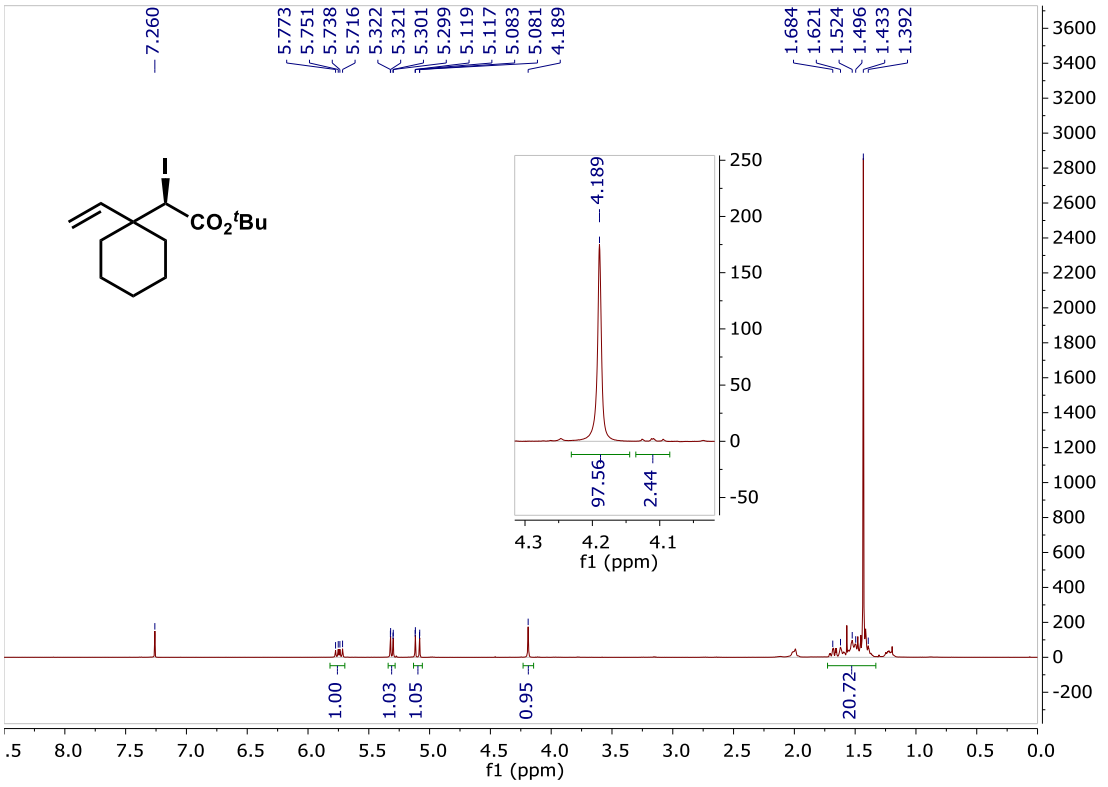


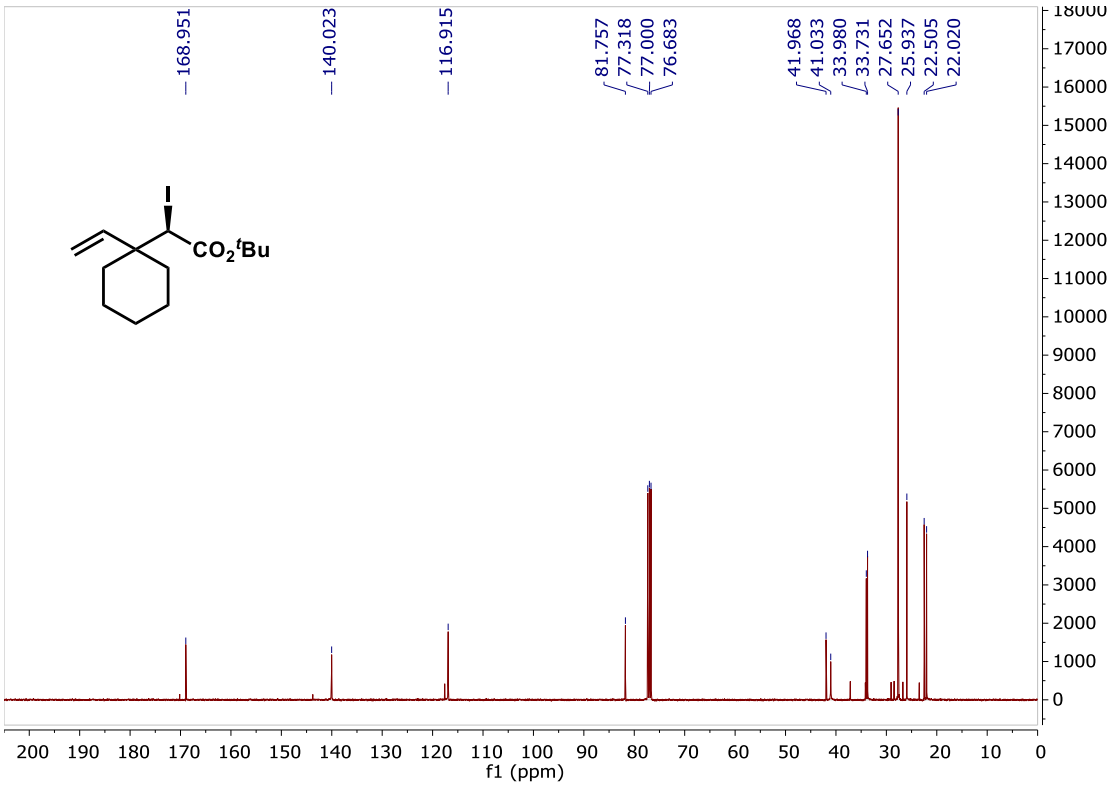
(+)-*tert*-Butyl (*R*)-2-iodo-2-(1-vinylcyclopentyl)acetate, 5t



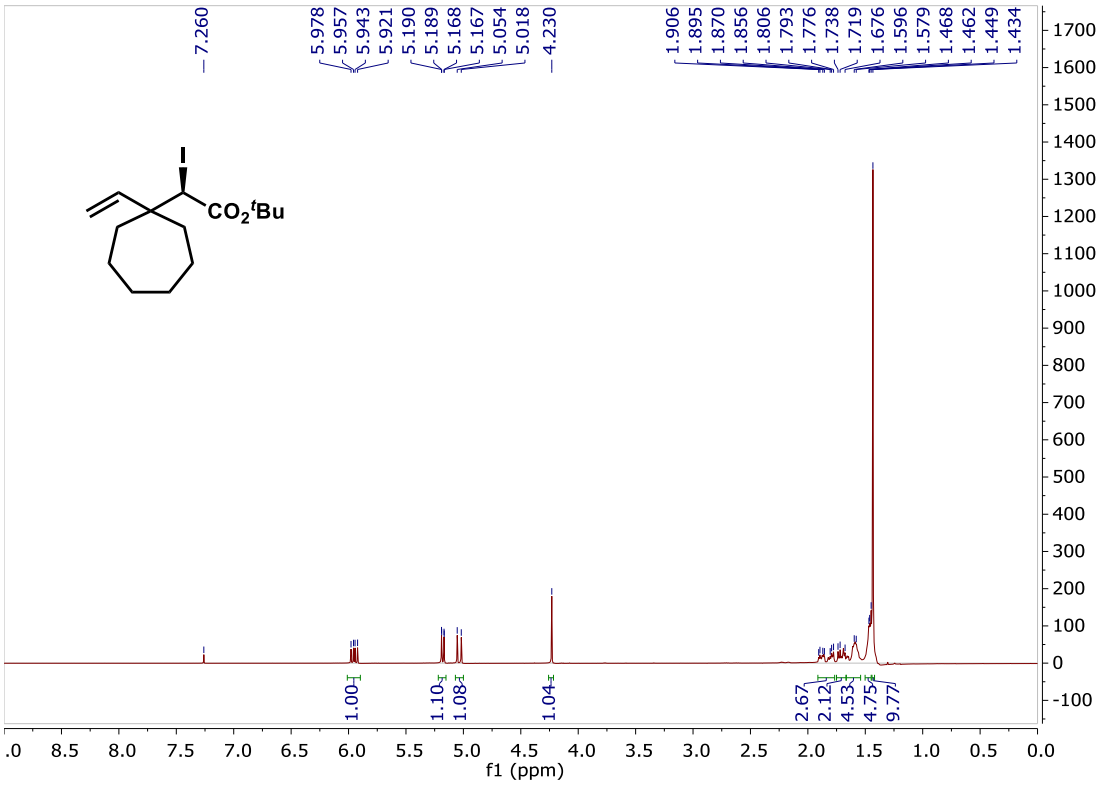


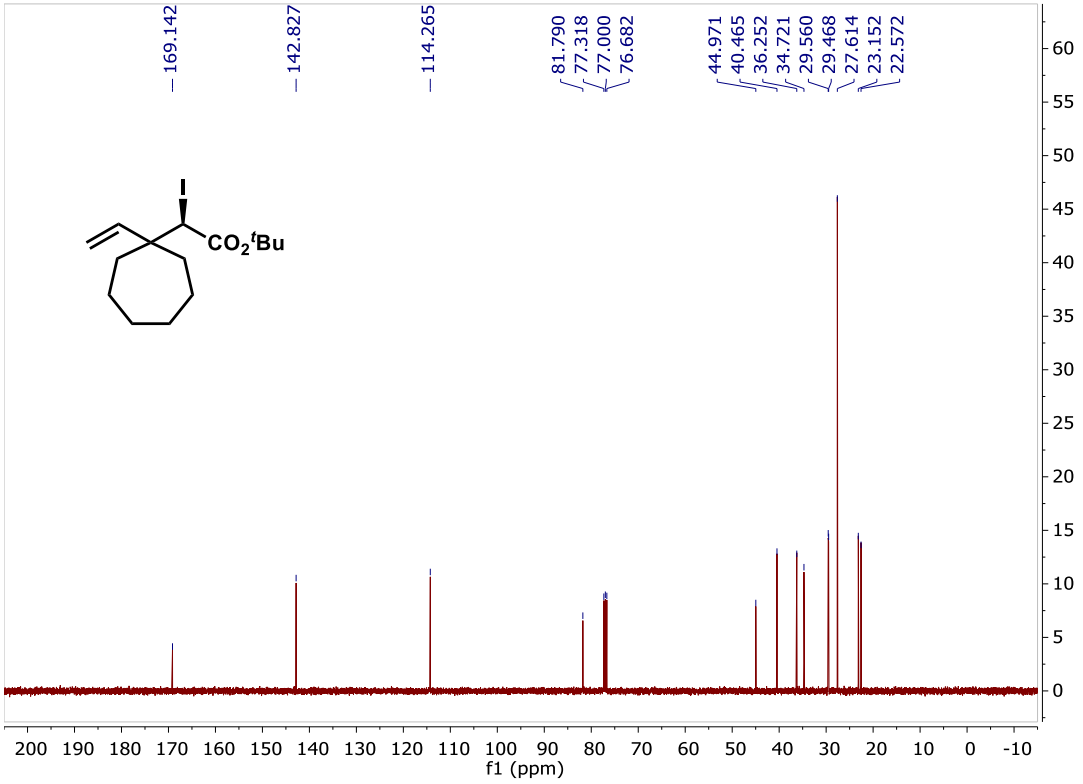
(+)-*tert*-Butyl (*R*)-2-iodo-2-(1-vinylcyclohexyl)acetate, 5u



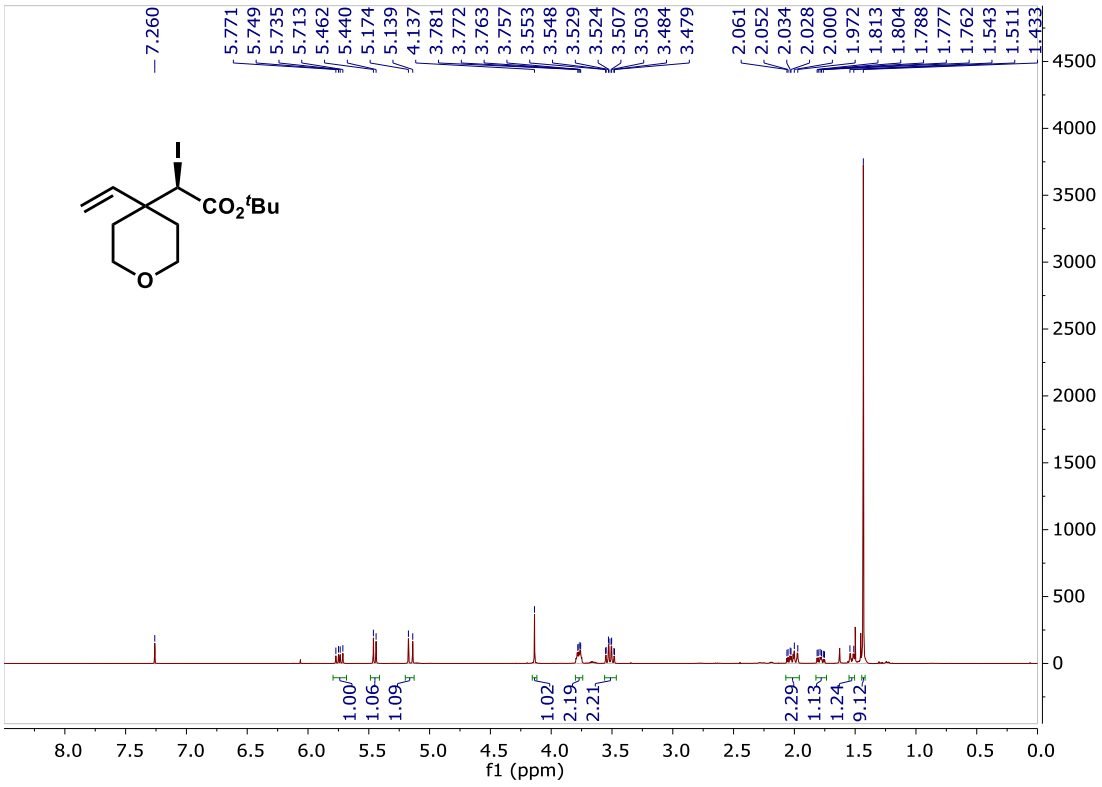


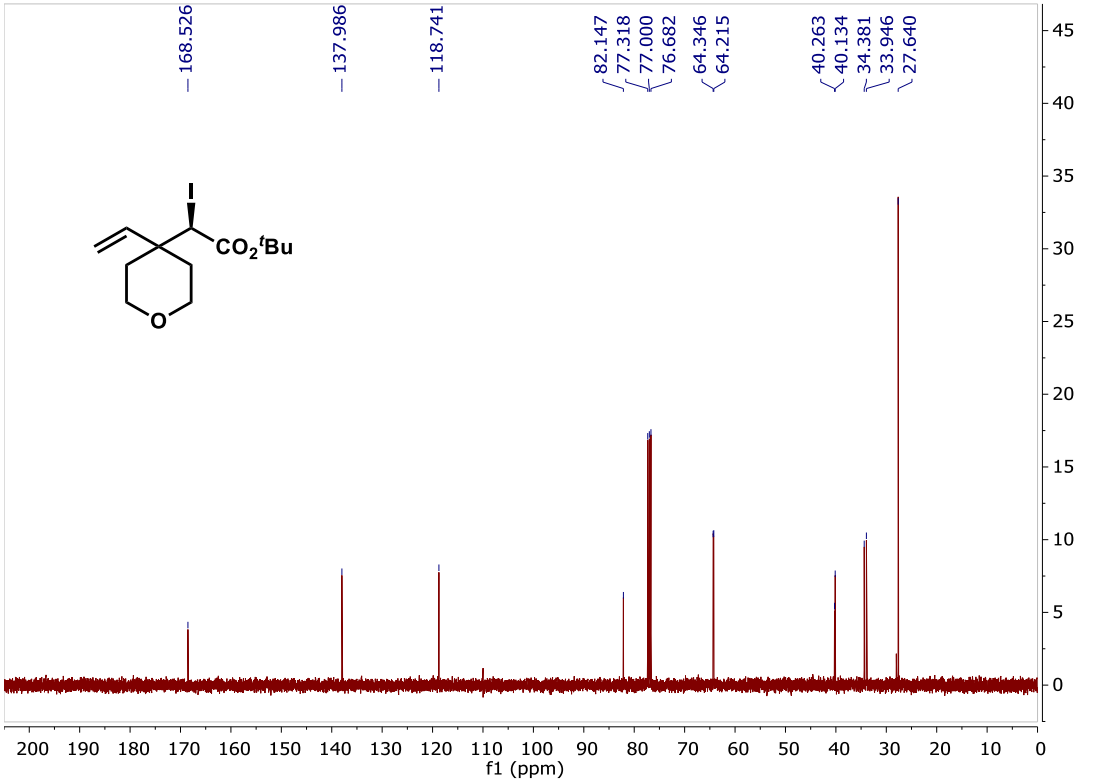
(+)-*tert*-Butyl (*R*)-2-iodo-2-(1-vinylcycloheptyl)acetate, 5v



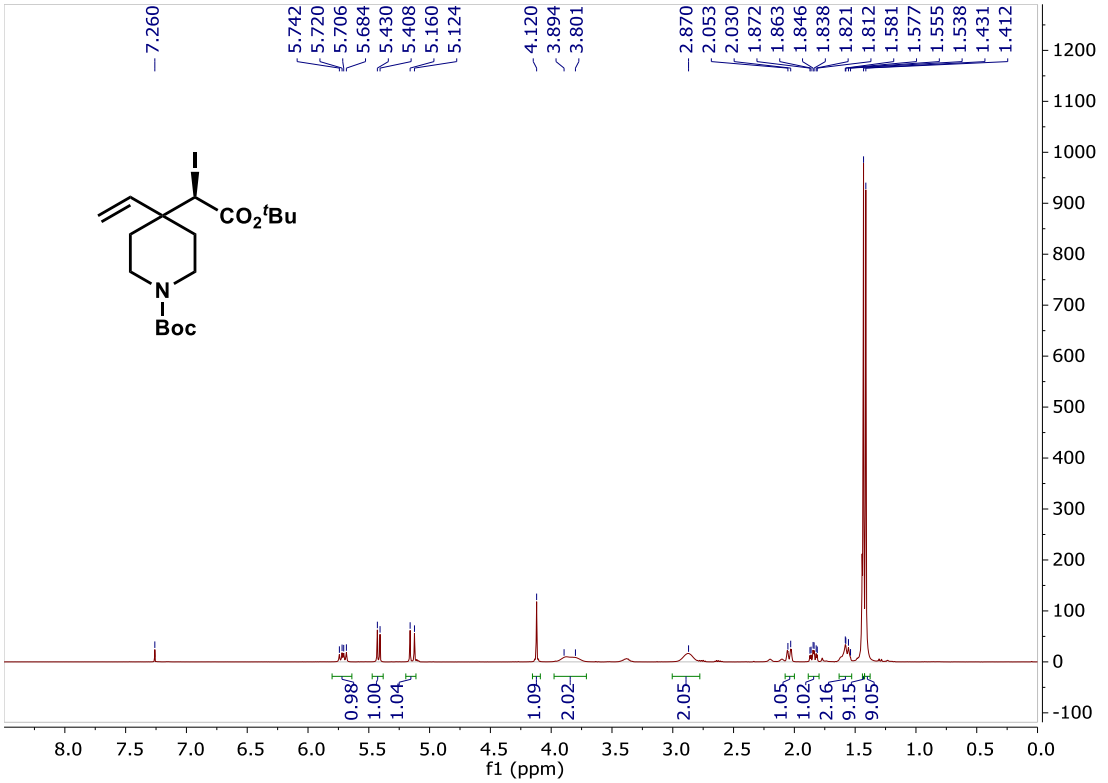


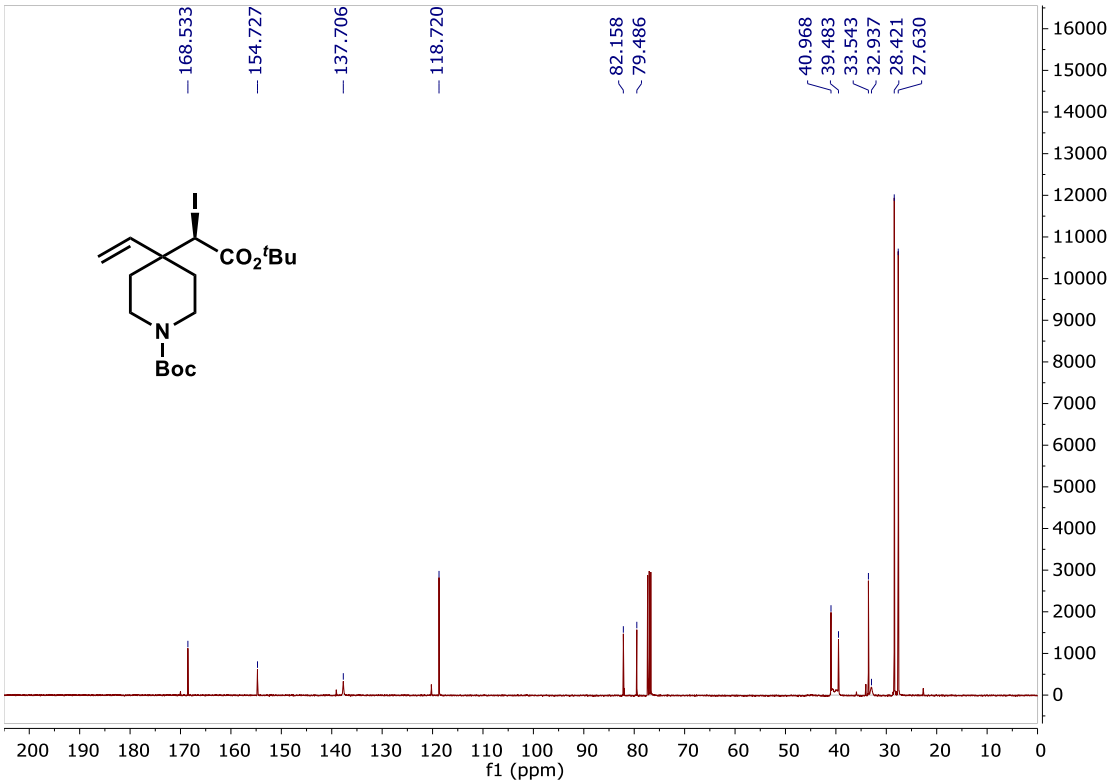
(+)-*tert*-Butyl (*R*)-2-iodo-2-(4-vinyltetrahydro-2H-pyran-4-yl)acetate, 5w



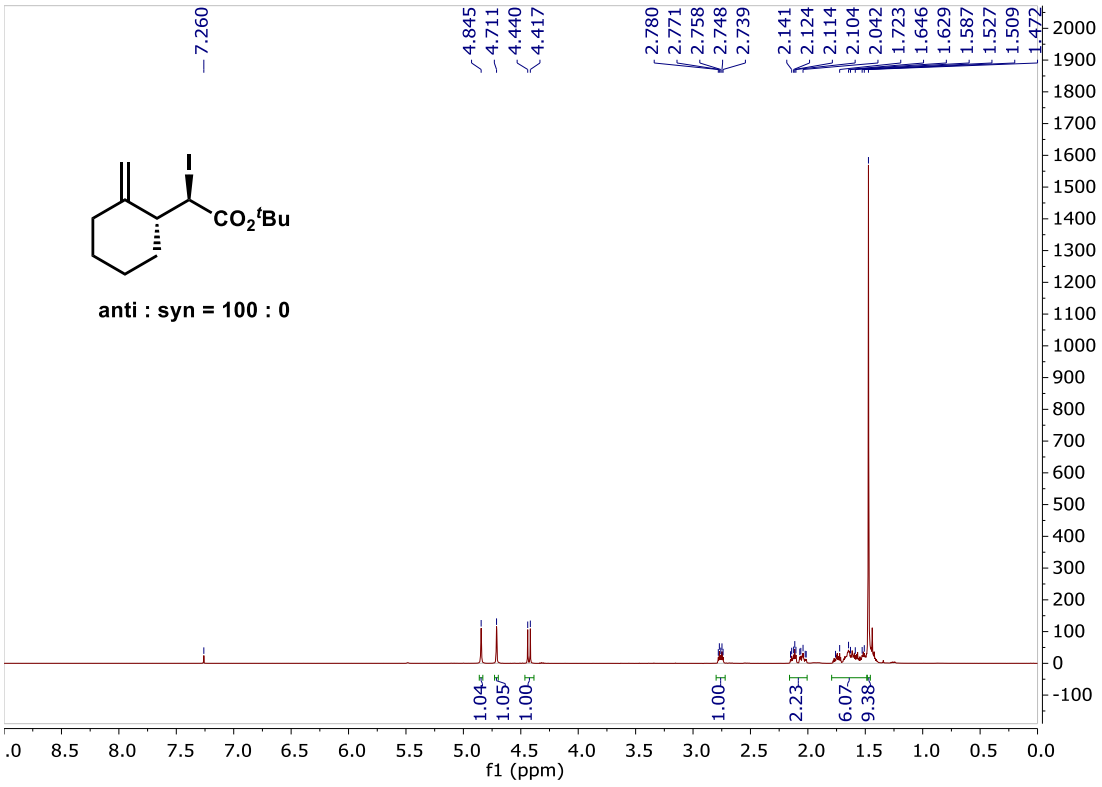


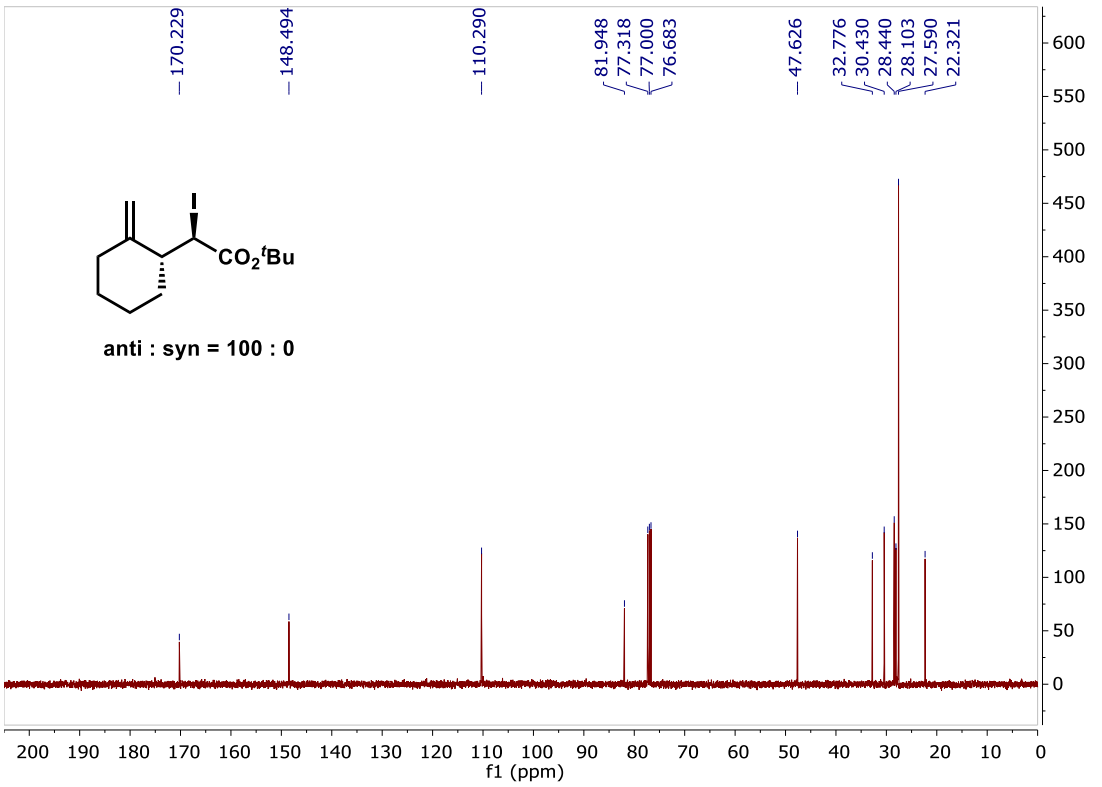
(+)-*tert*-Butyl
(*R*)-4-(2-(*tert*-butoxy)-1-iodo-2-oxoethyl)-4-vinylpiperidine-1-carboxylate, 5x



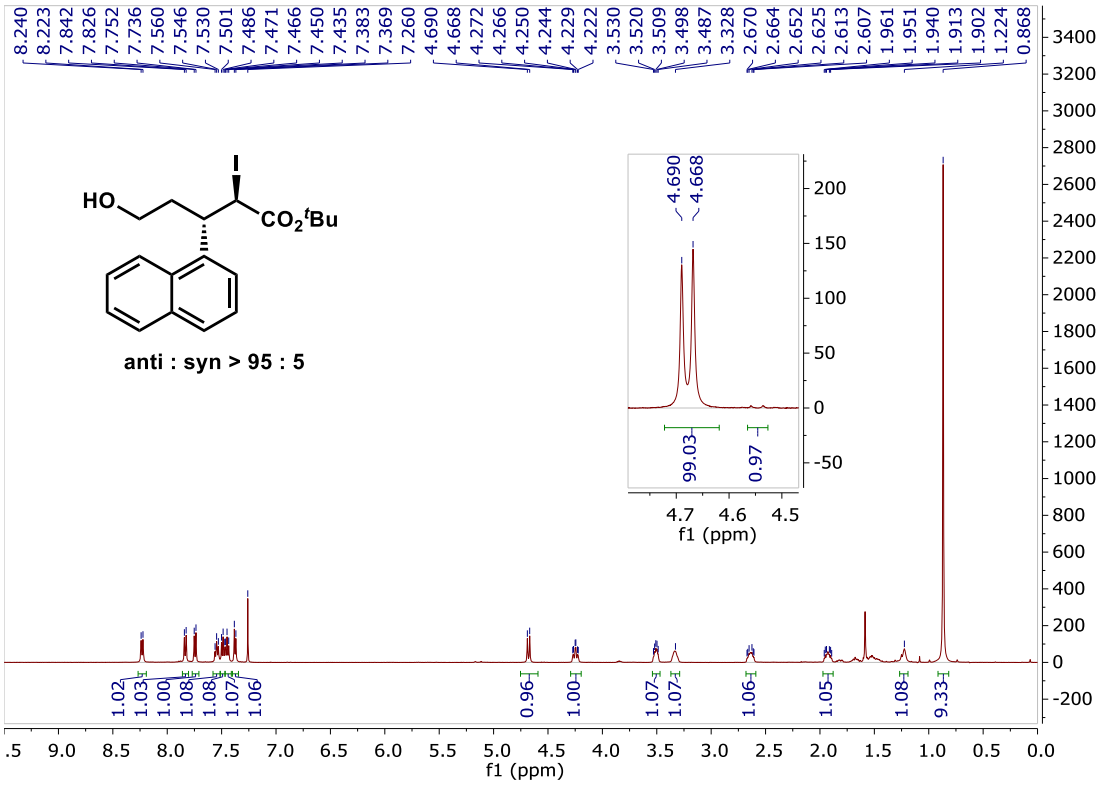


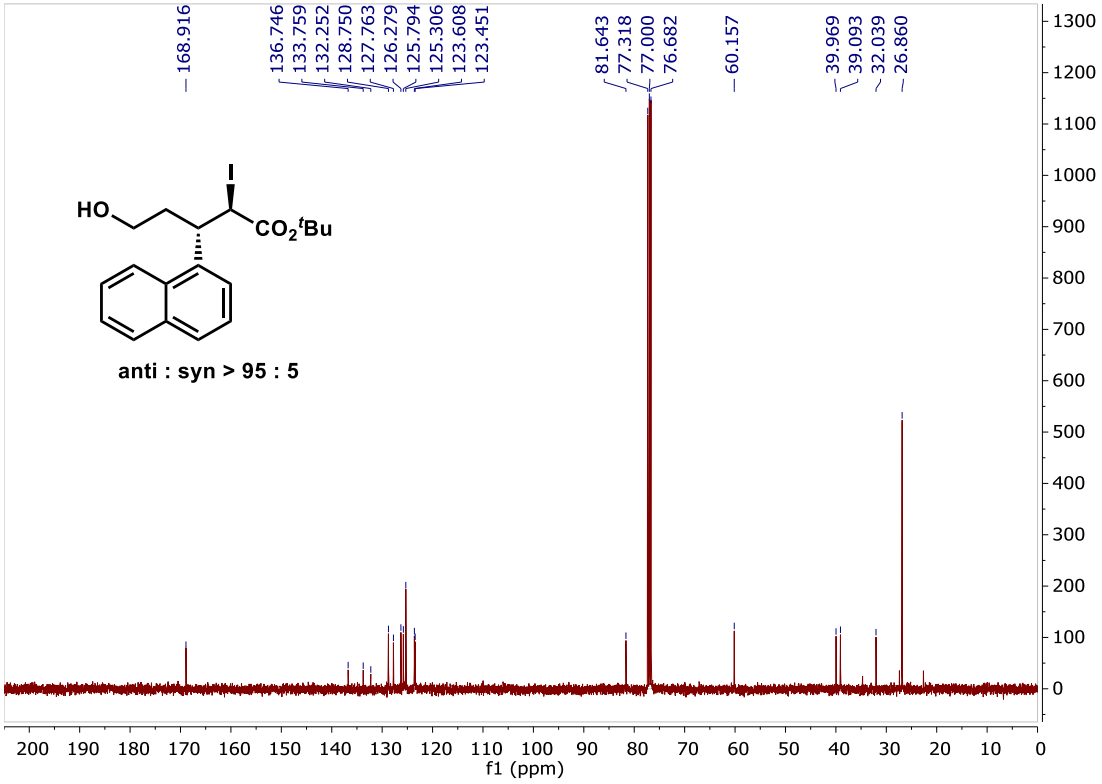
(+)-*tert*-Butyl (*R*)-2-iodo-2-((*R*)-2-methylenecyclohexyl)acetate, 5y



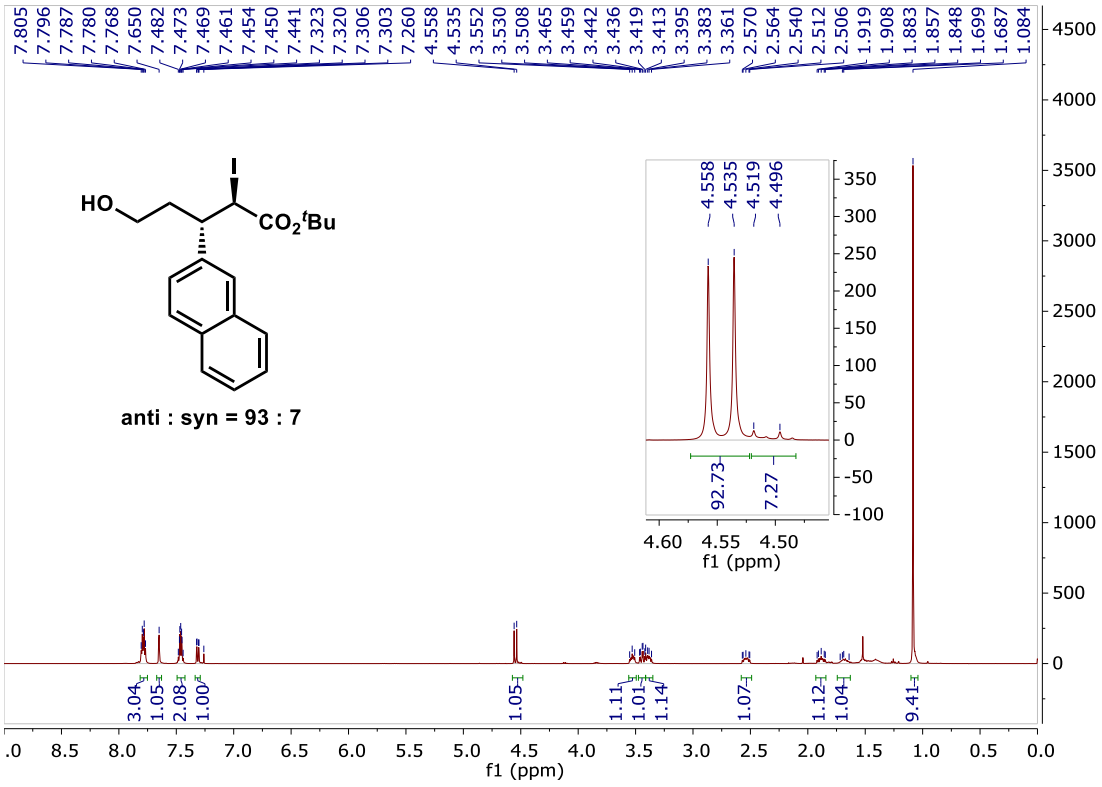


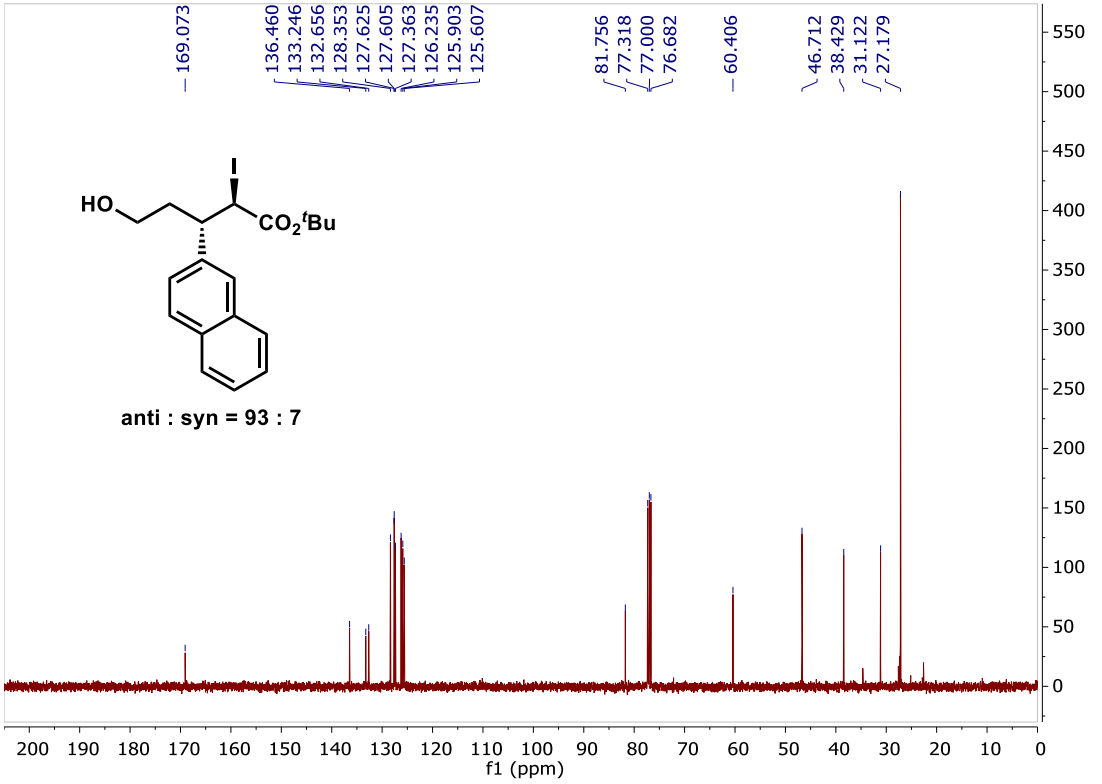
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(naphthalen-1-yl)pentanoate, 6c



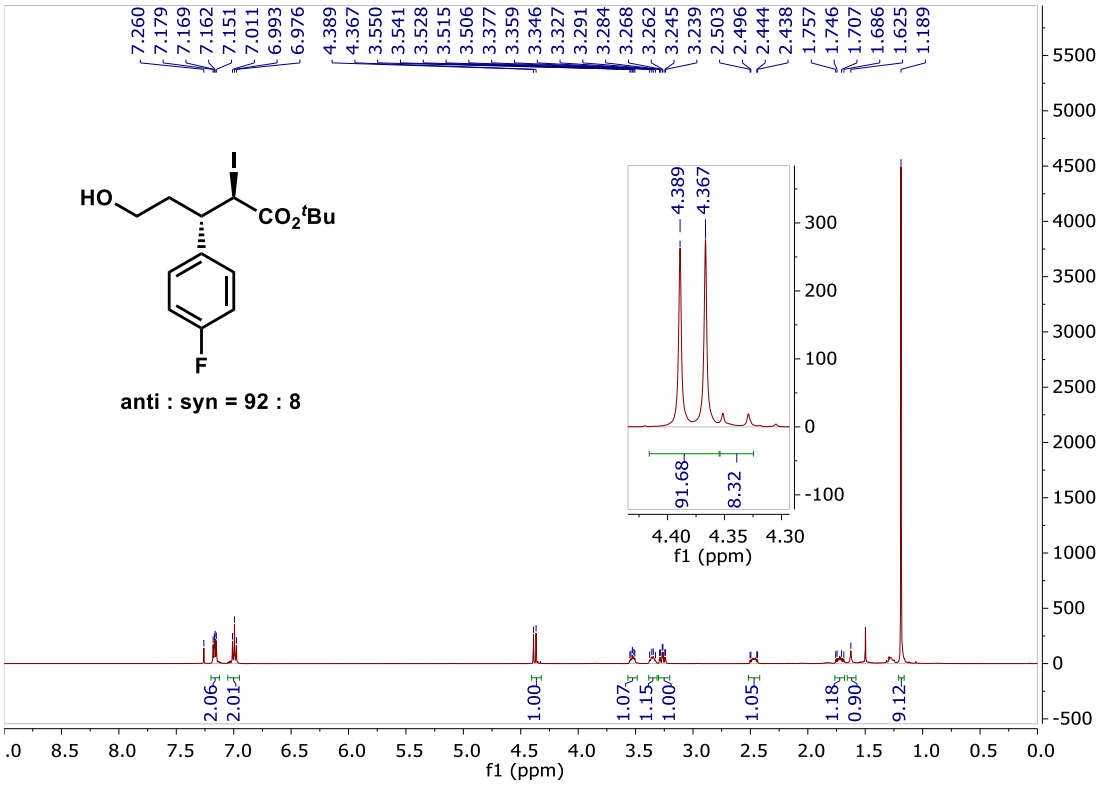


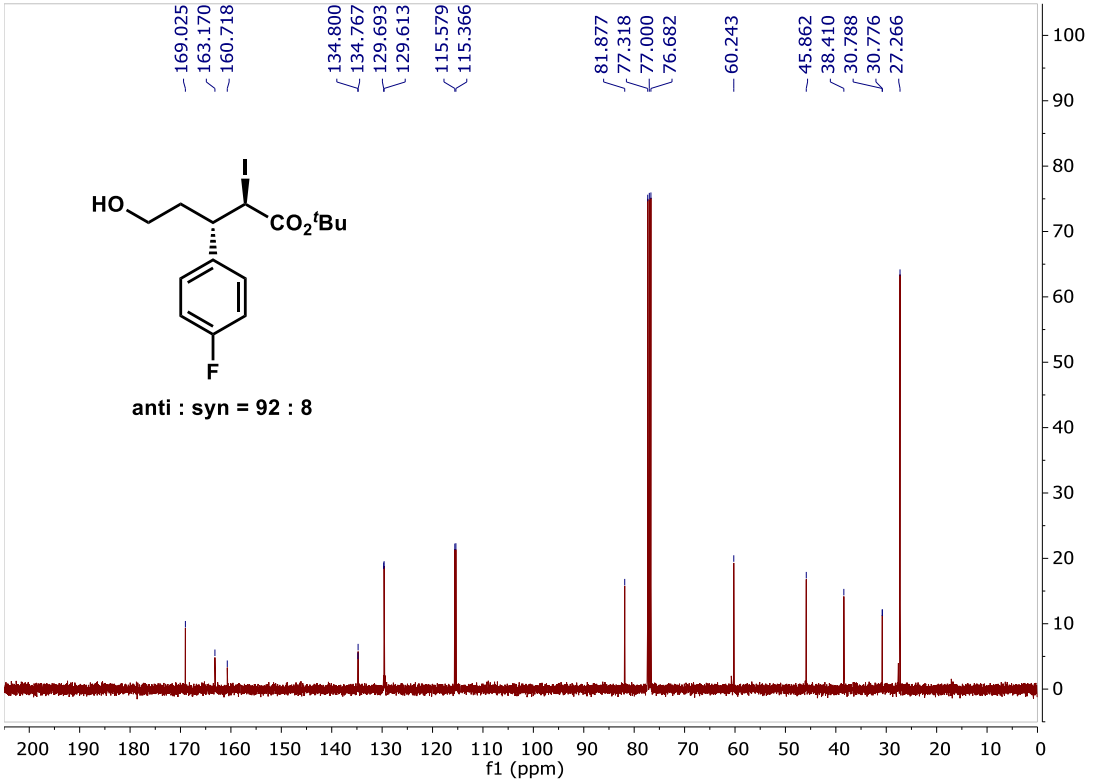
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(naphthalen-2-yl)pentanoate, 6d



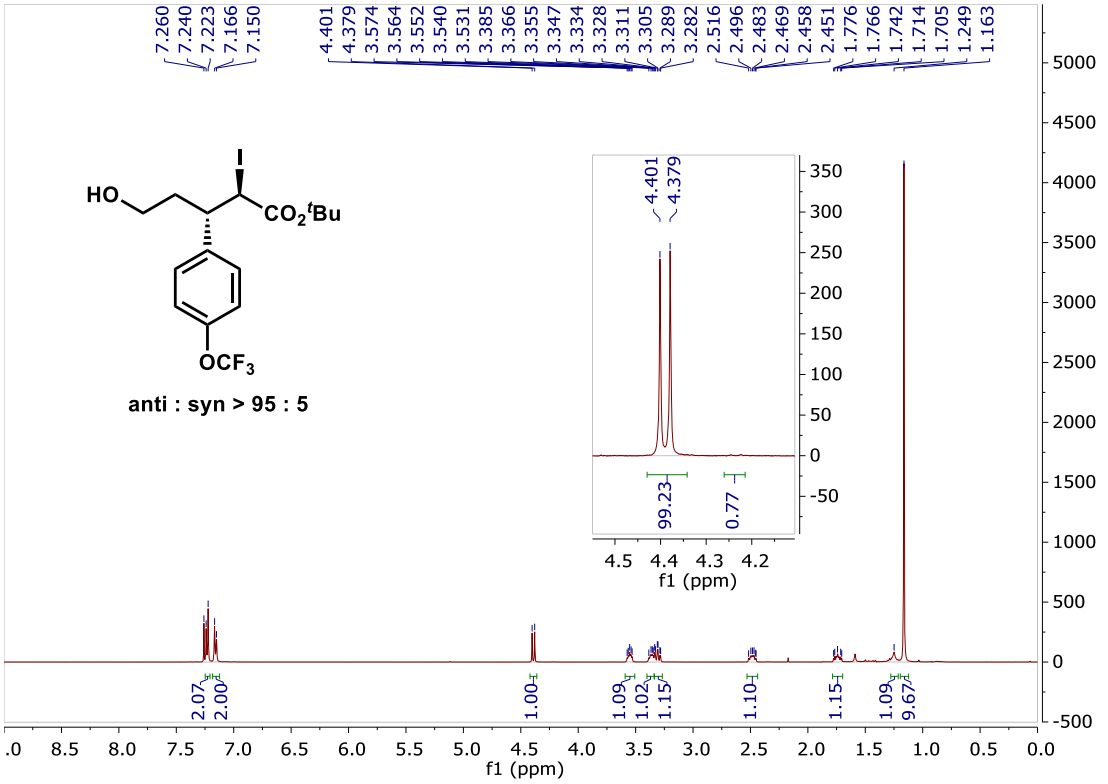


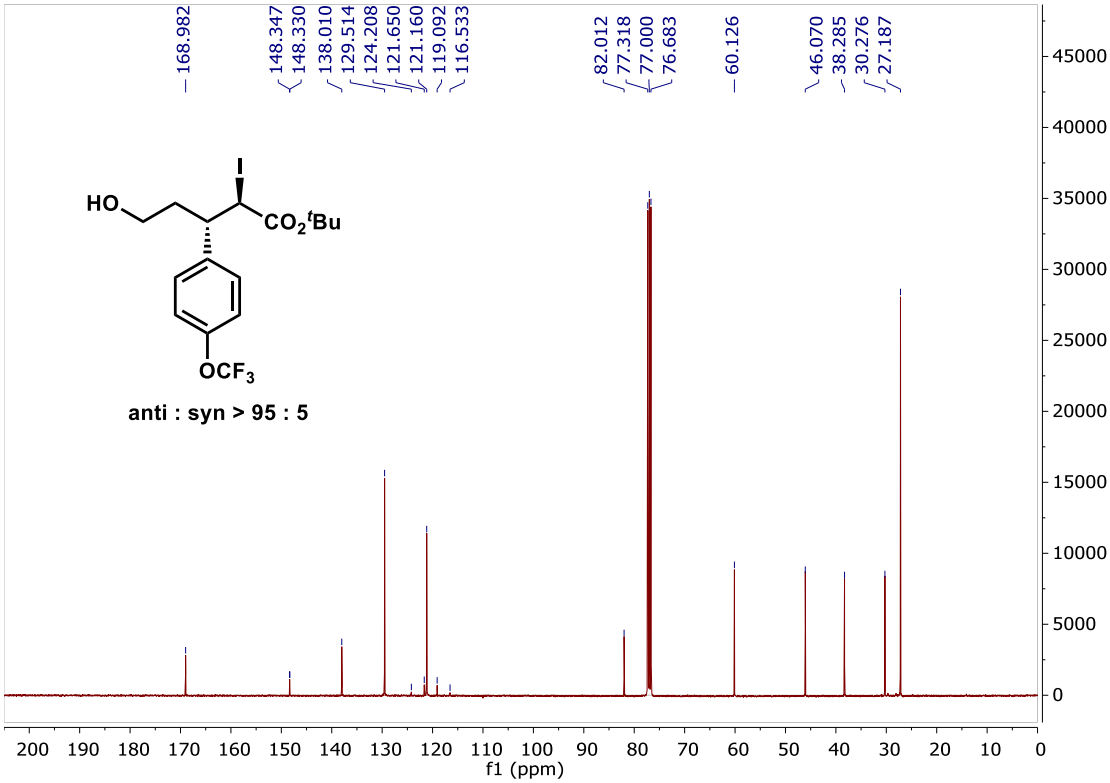
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-fluorophenyl)-5-hydroxy-2-iodopentanoate, 6h



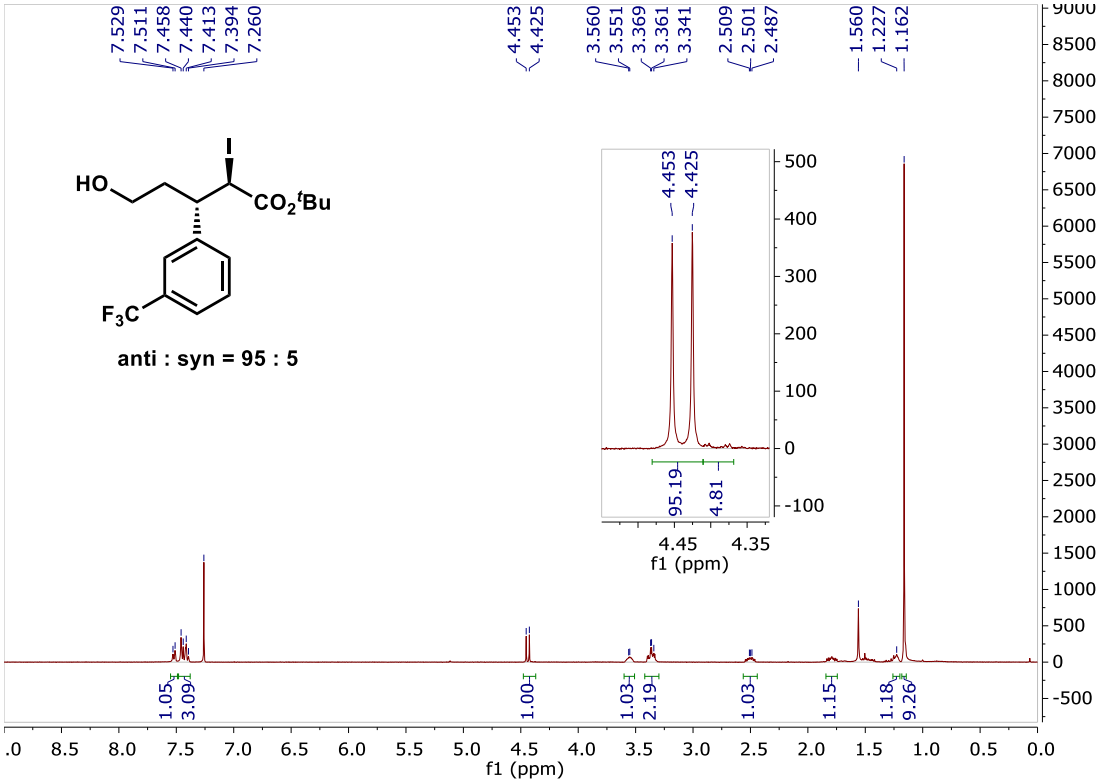


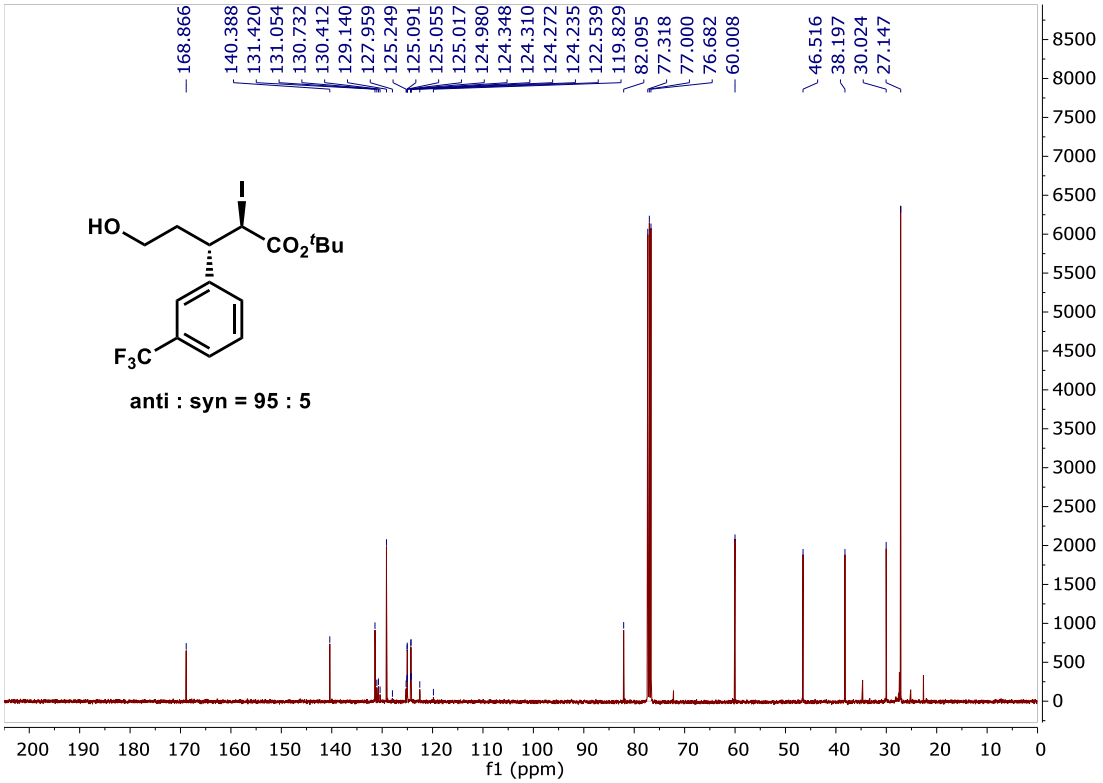
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(4-(trifluoromethoxy)phenyl)pentanoate, 6i



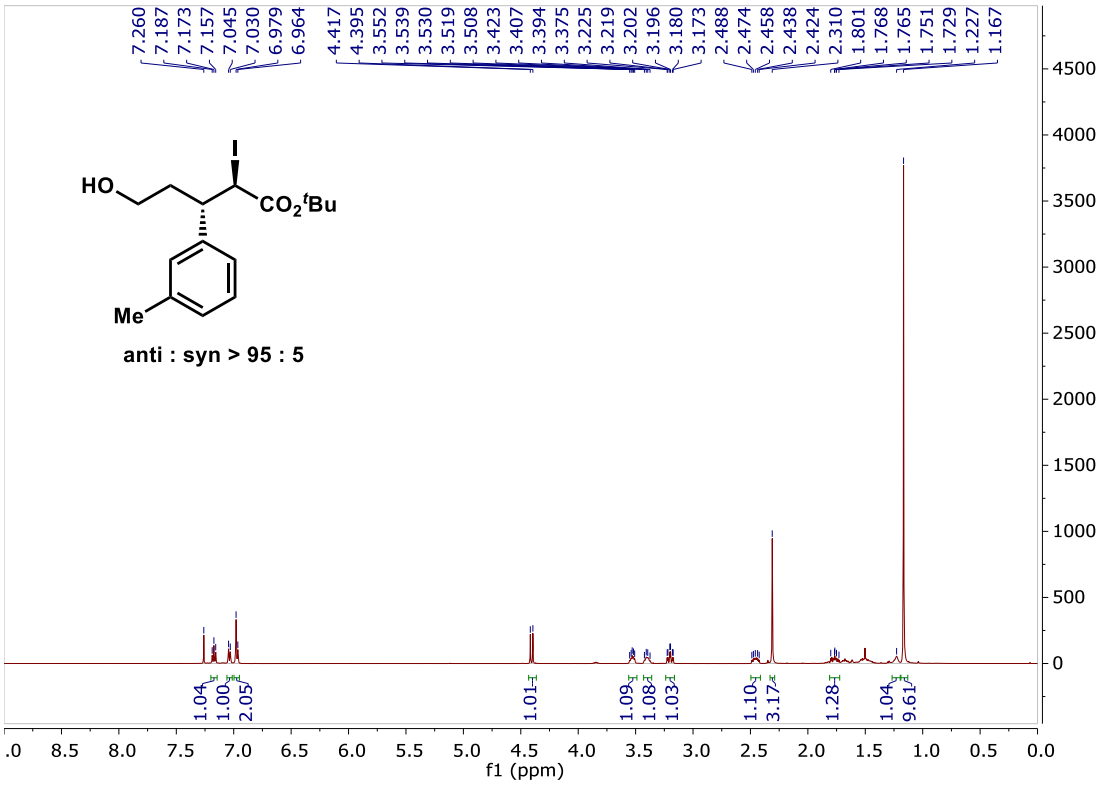


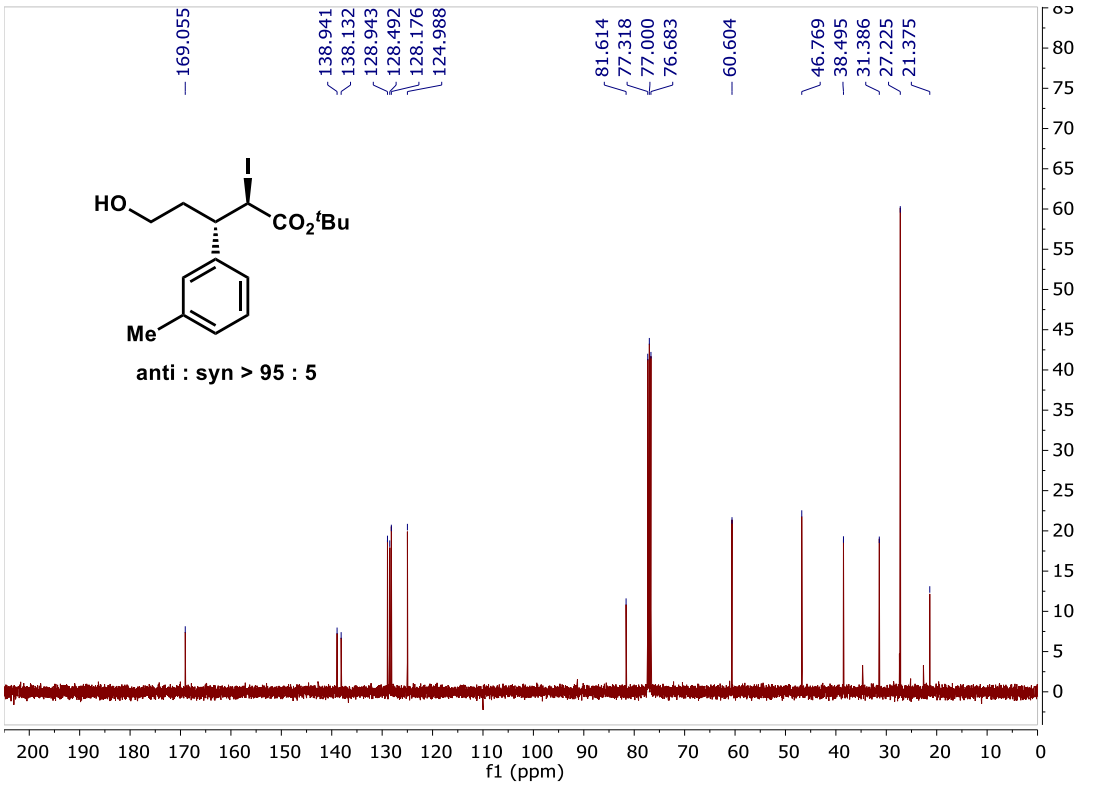
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(3-(trifluoromethyl)phenyl)pentanoate, 6j



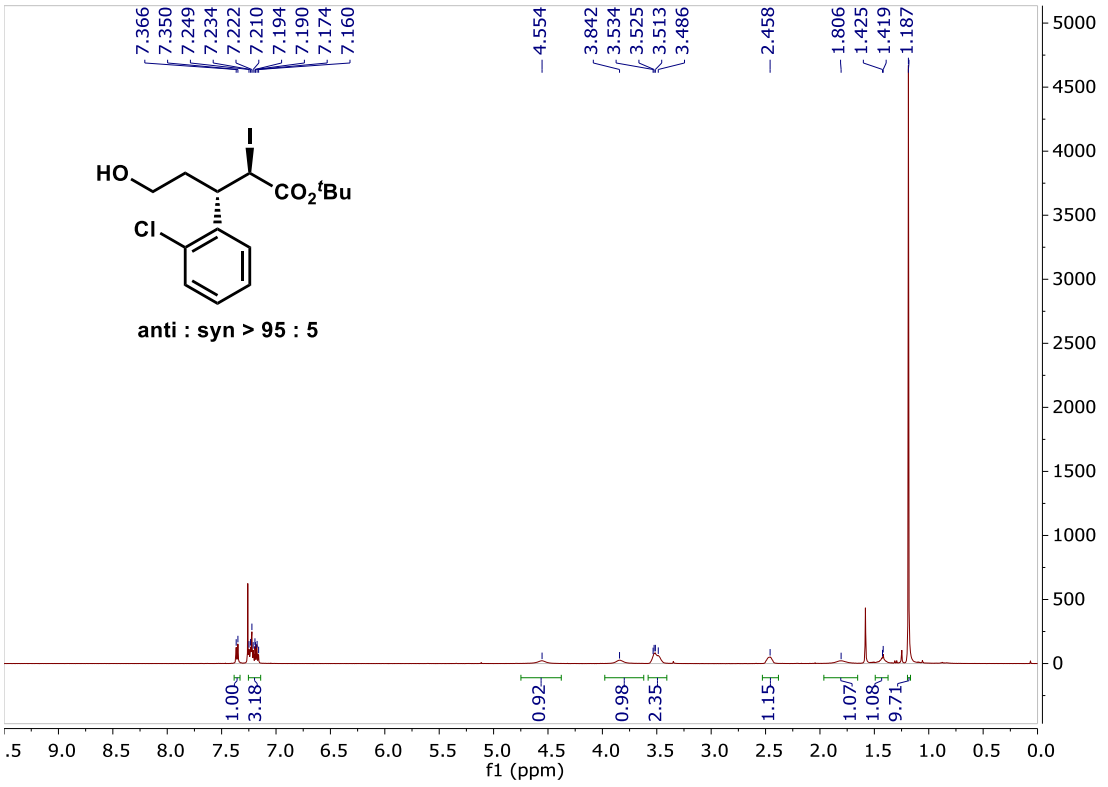


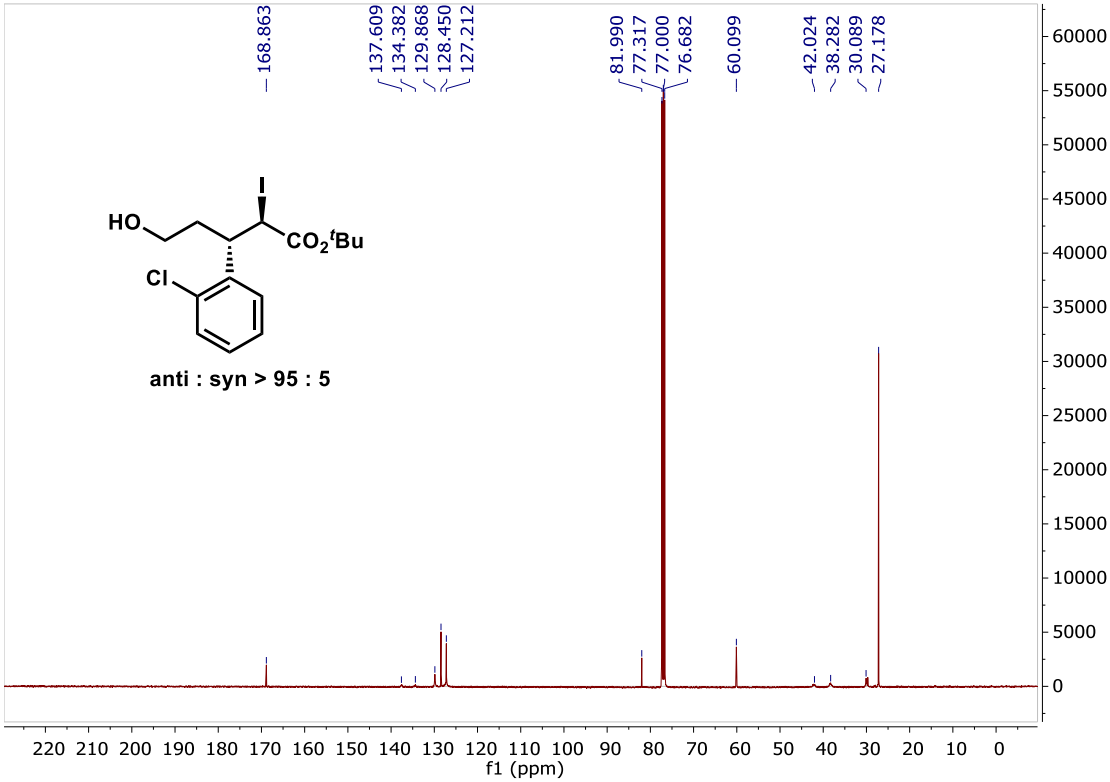
(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(*m*-tolyl)pentanoate, 6k



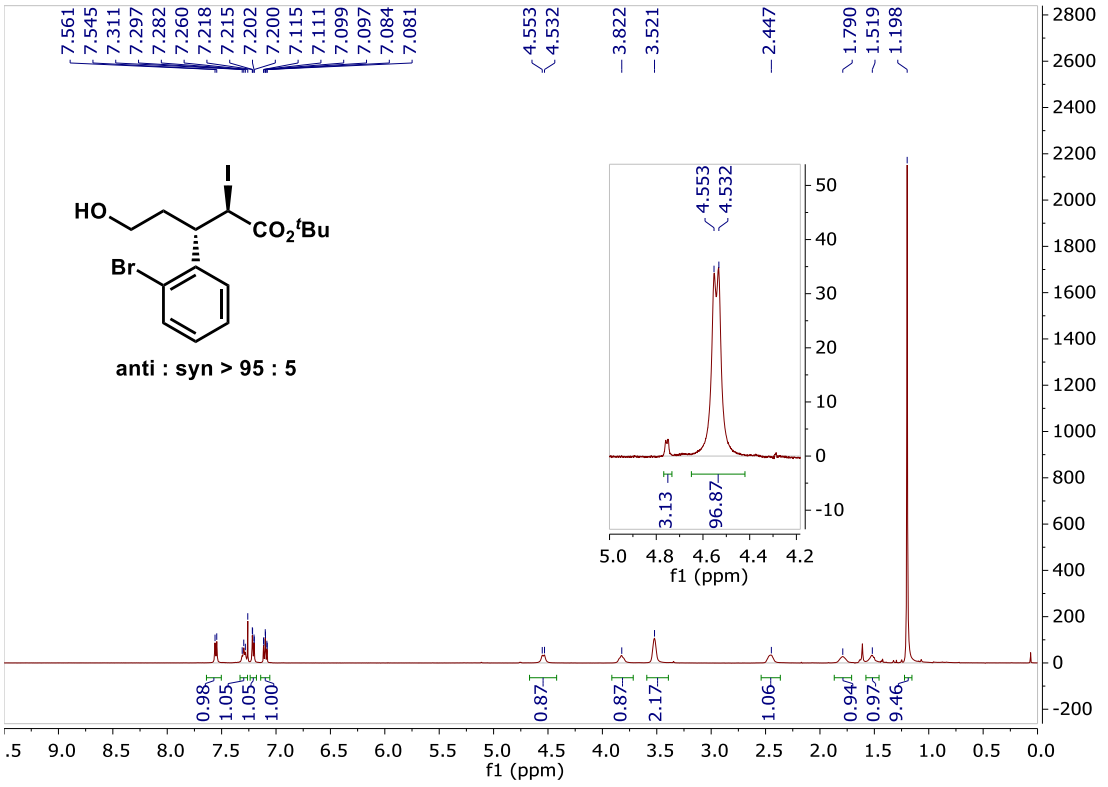


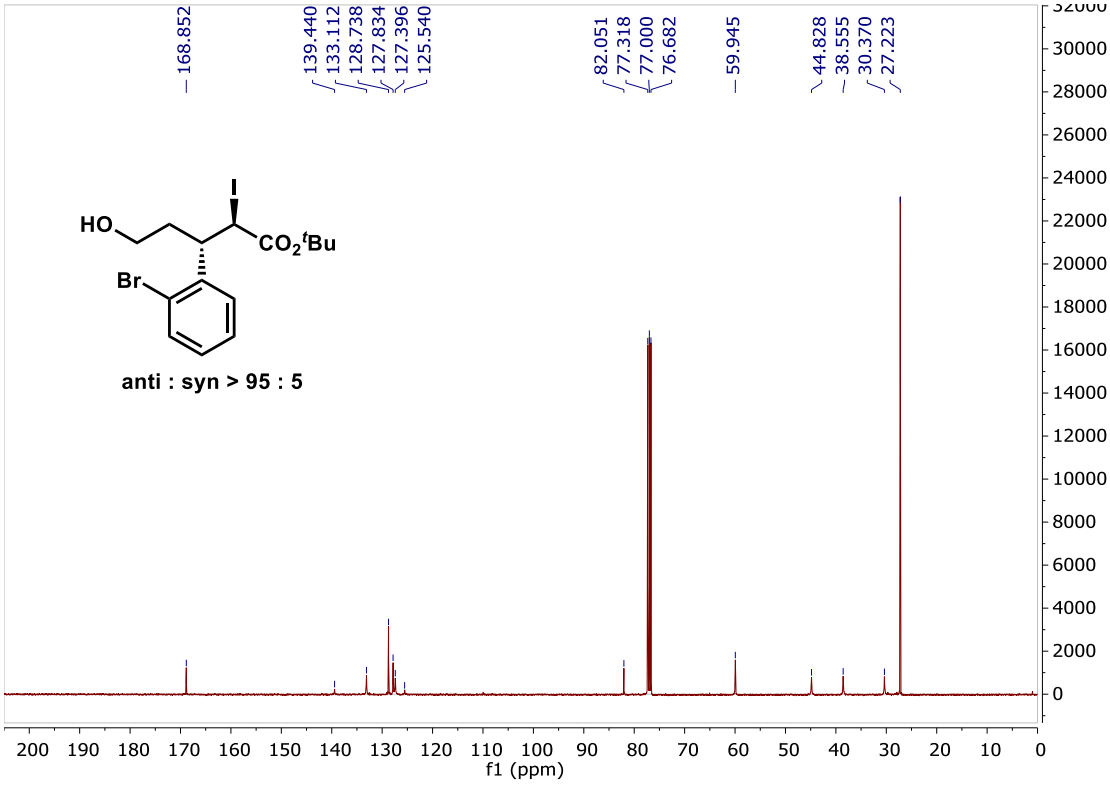
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-chlorophenyl)-5-hydroxy-2-iodopentanoate, 6l



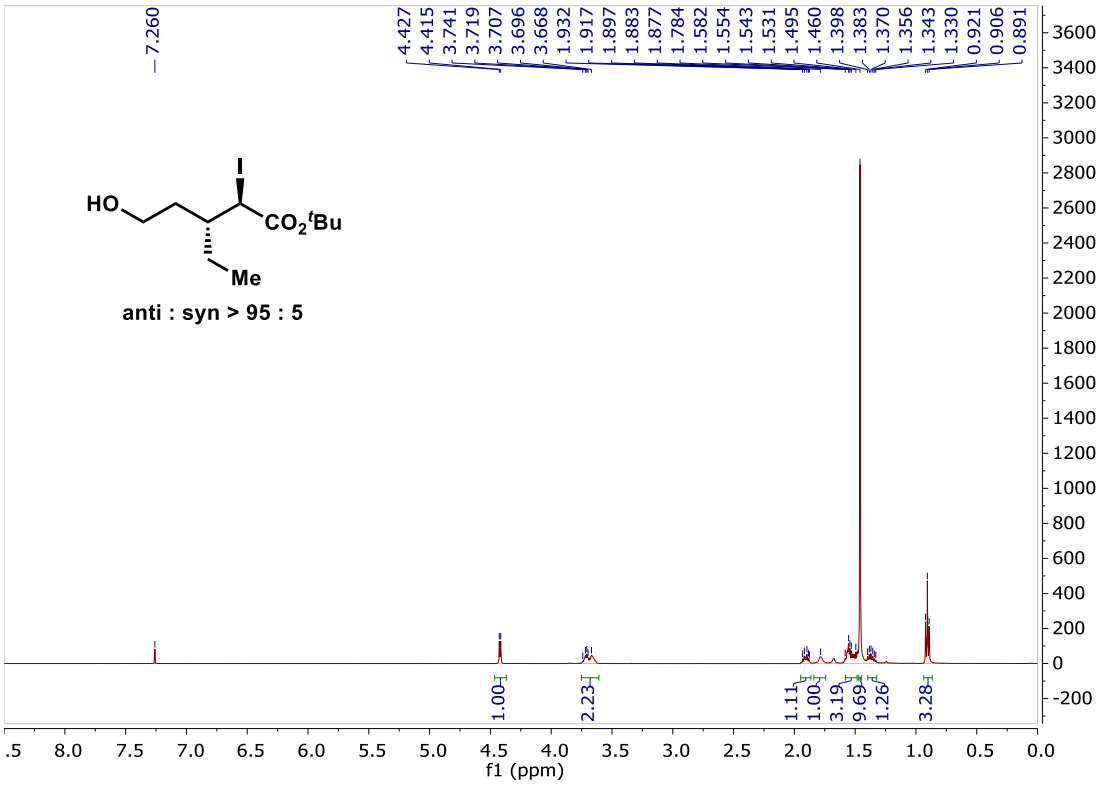


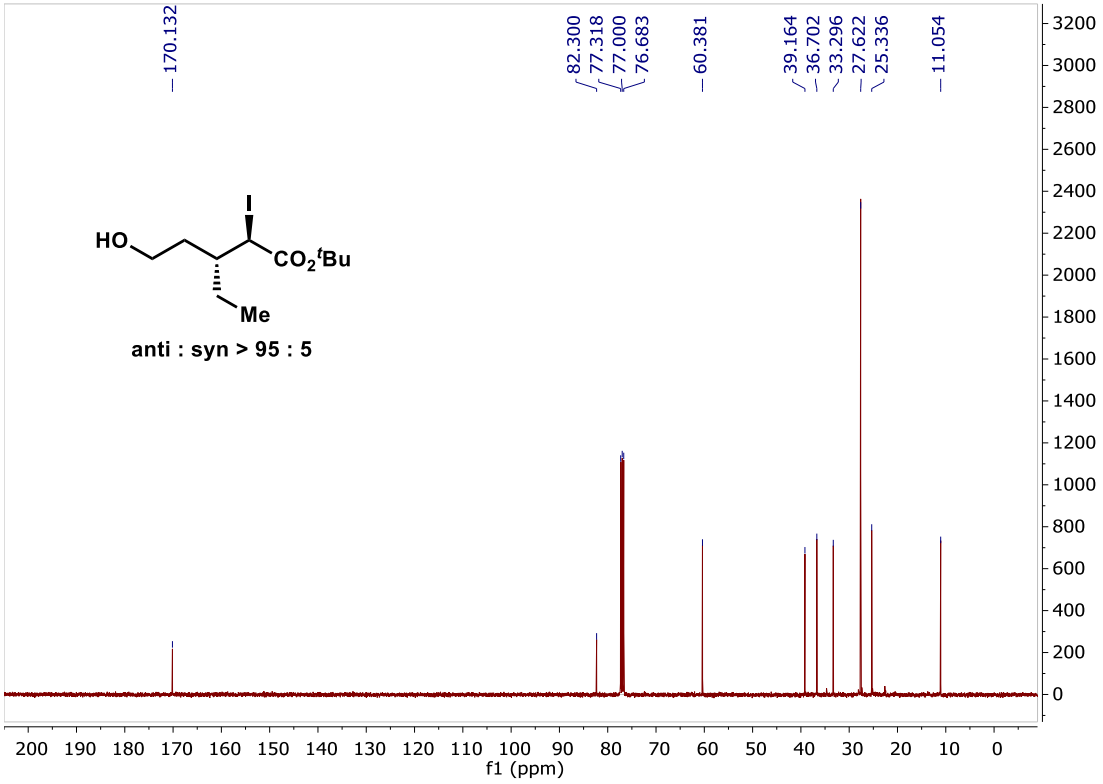
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-bromophenyl)-5-hydroxy-2-iodopentanoate, 6m



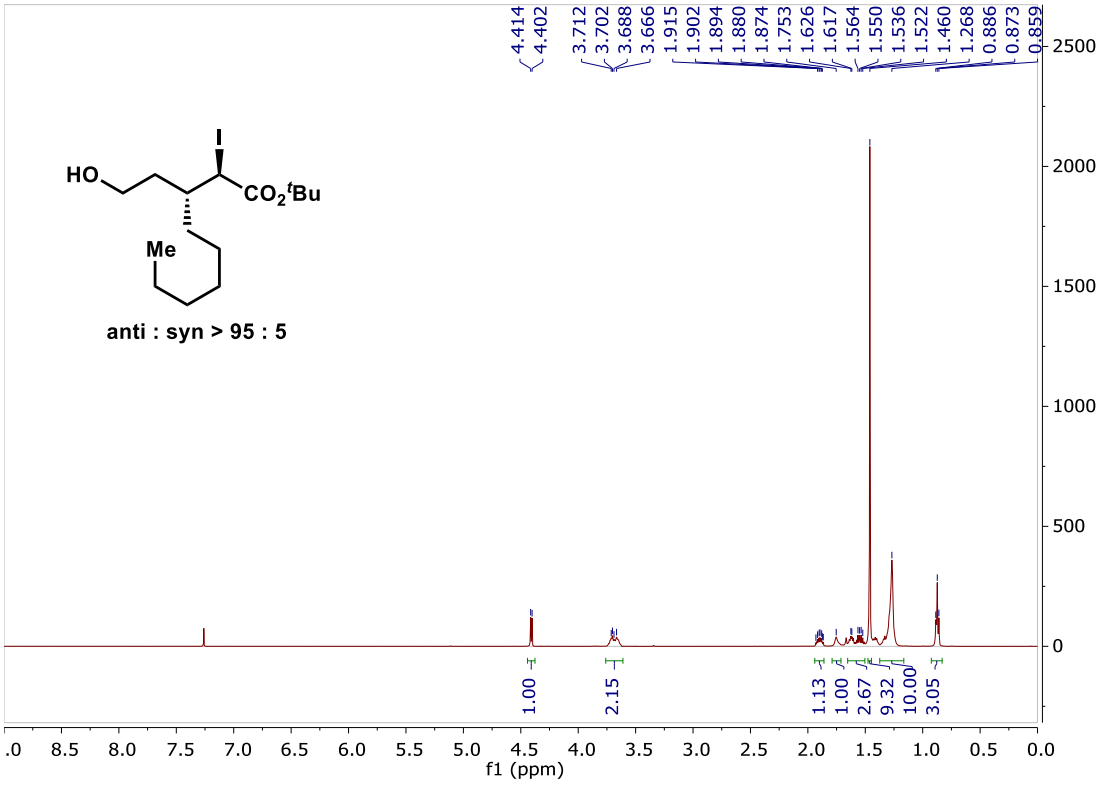


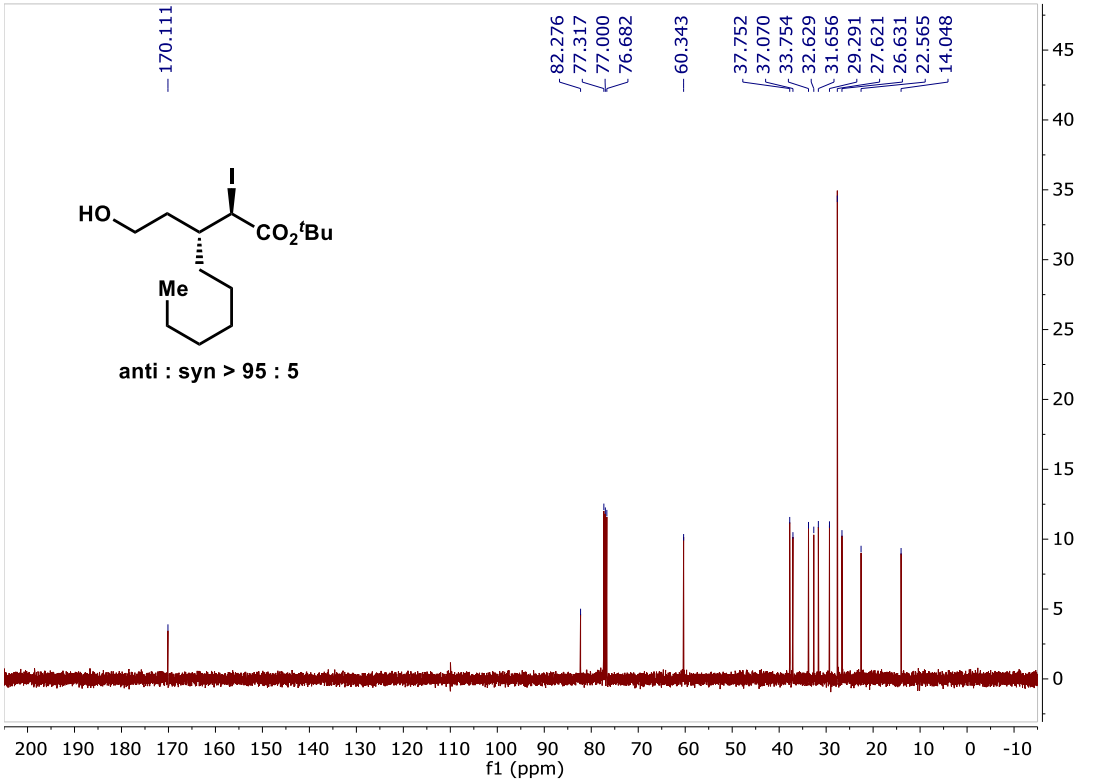
(+)-*tert*-Butyl (2*R*, 3*R*)-3-ethyl-5-hydroxy-2-iodopentanoate, 6n



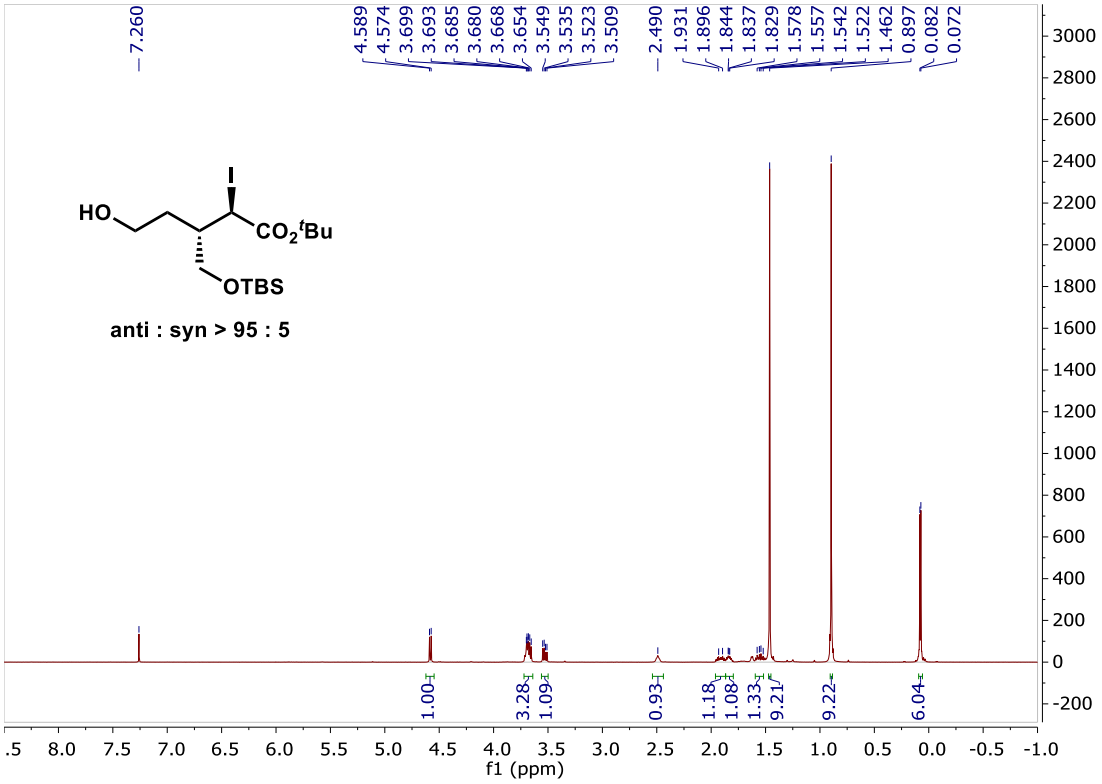


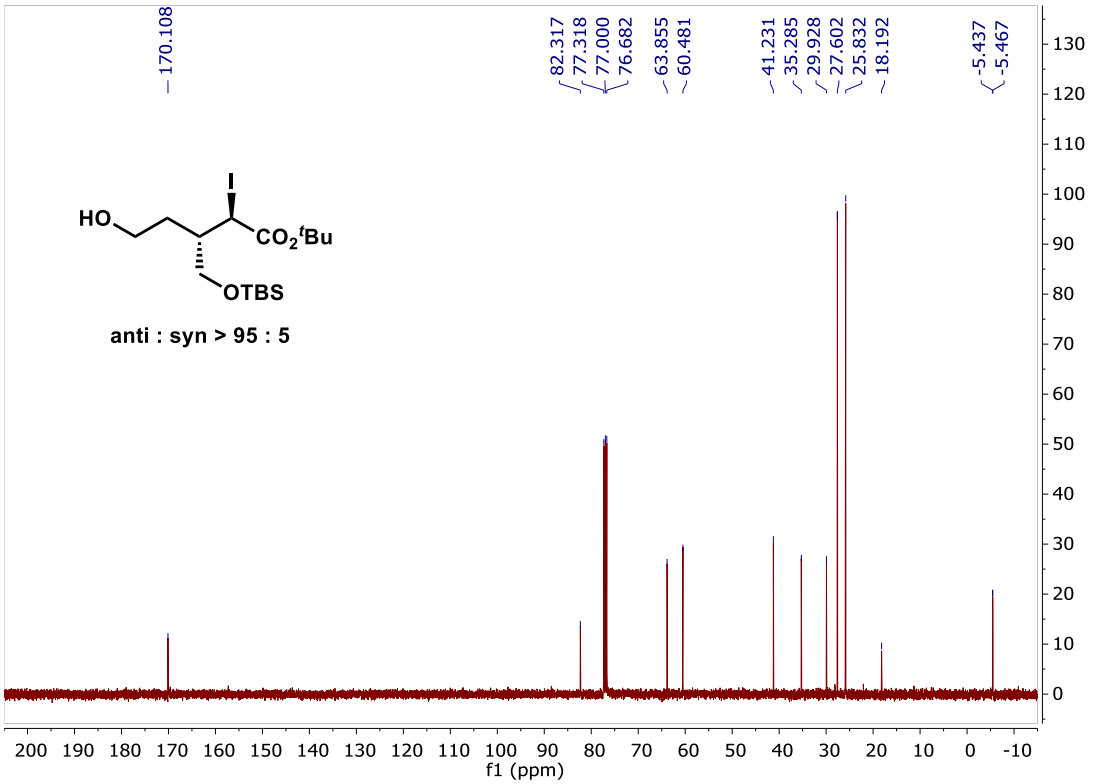
(+)-*tert*-Butyl (2*R*, 3*R*)-3-(2-hydroxyethyl)-2-iodononanoate, 6o



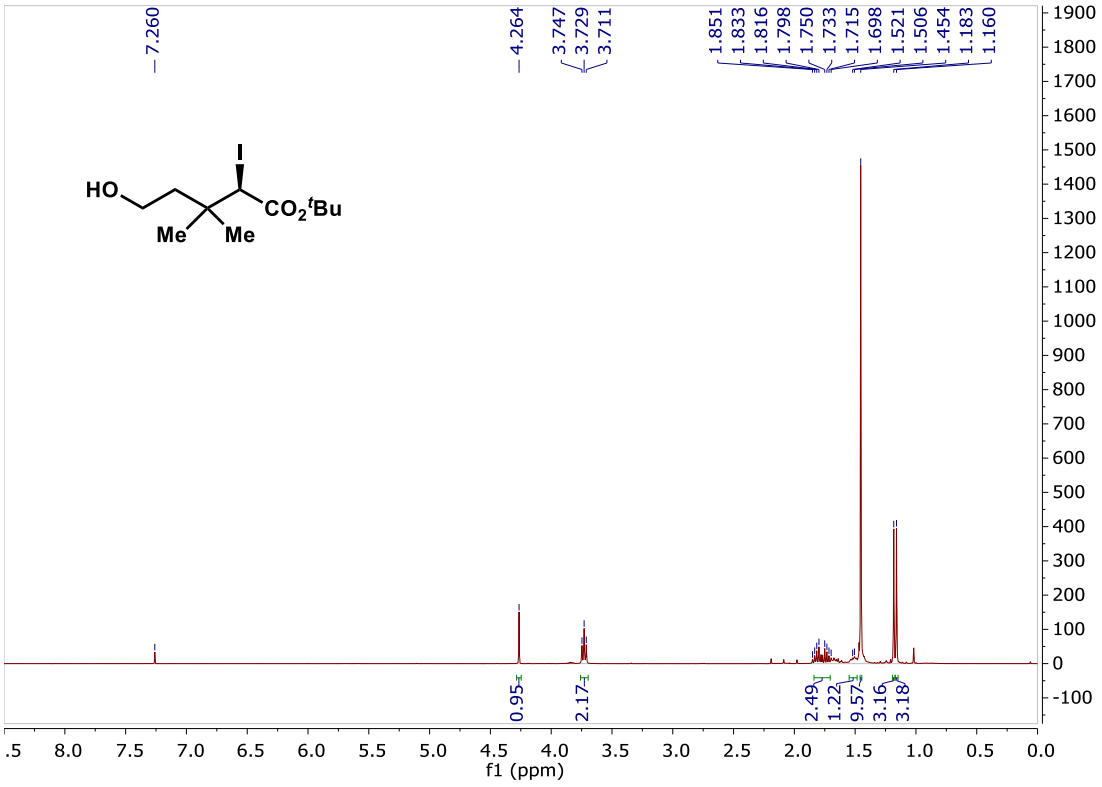


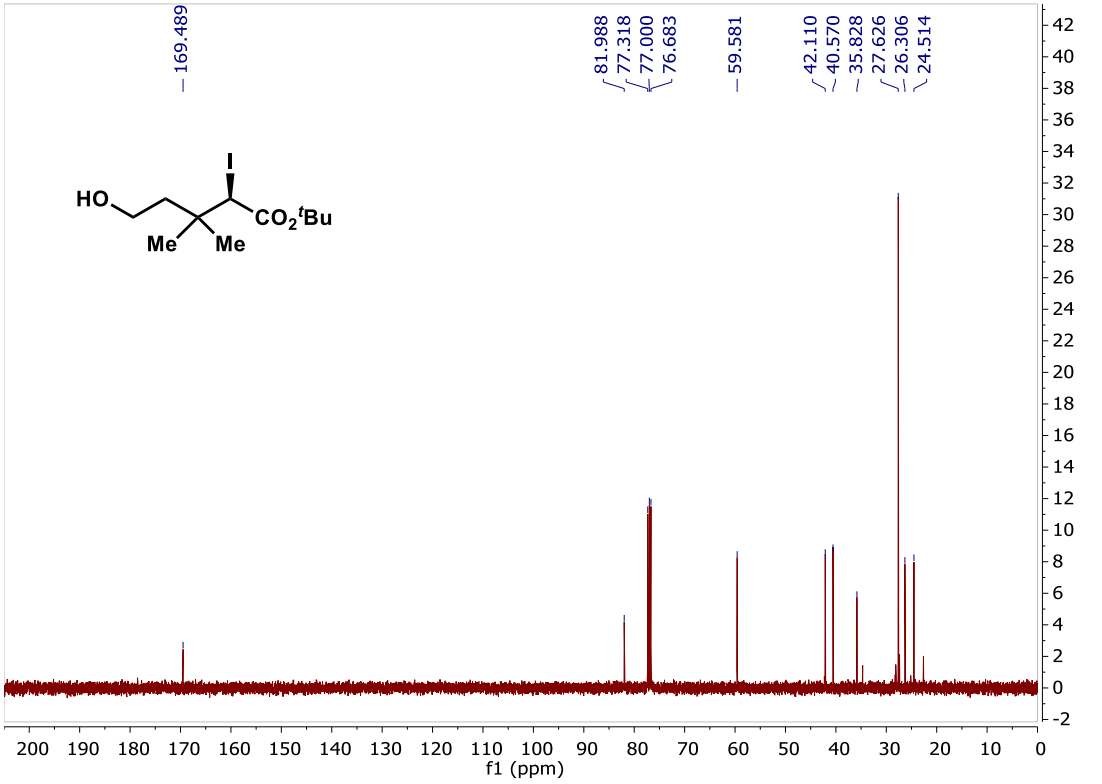
(+)-*tert*-Butyl (2*R*, 3*S*)-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-hydroxy-2-iodopentanoate, 6p



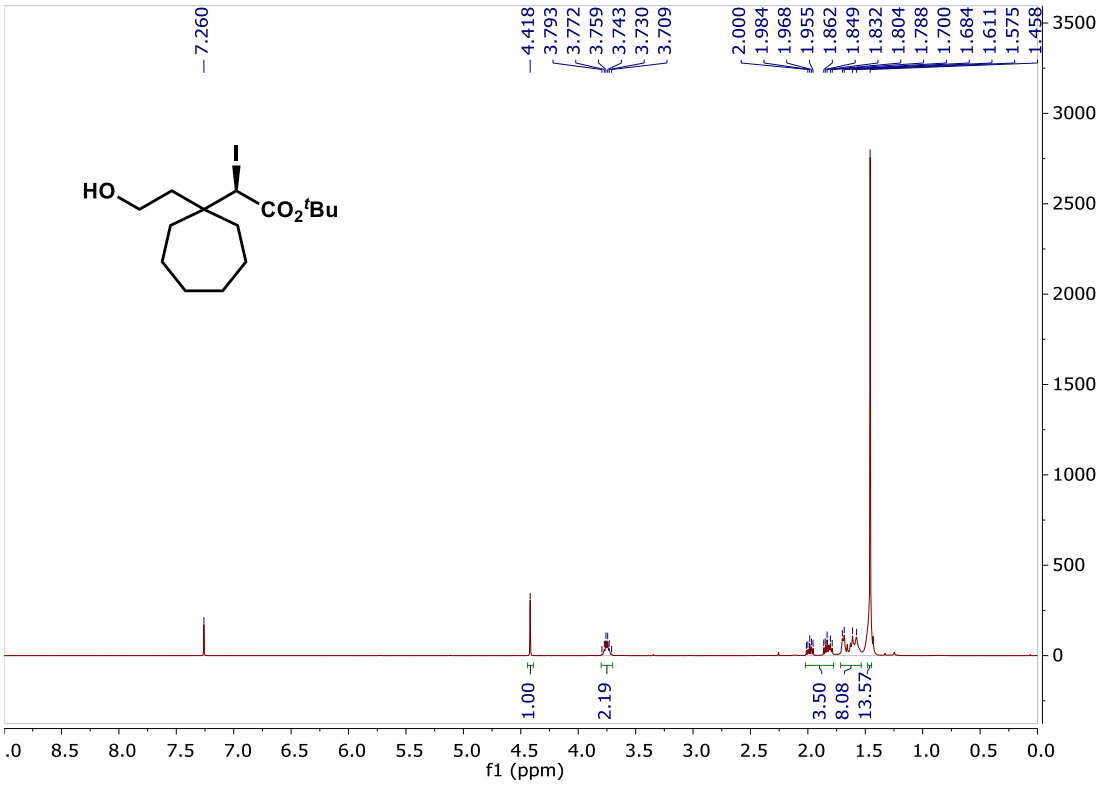


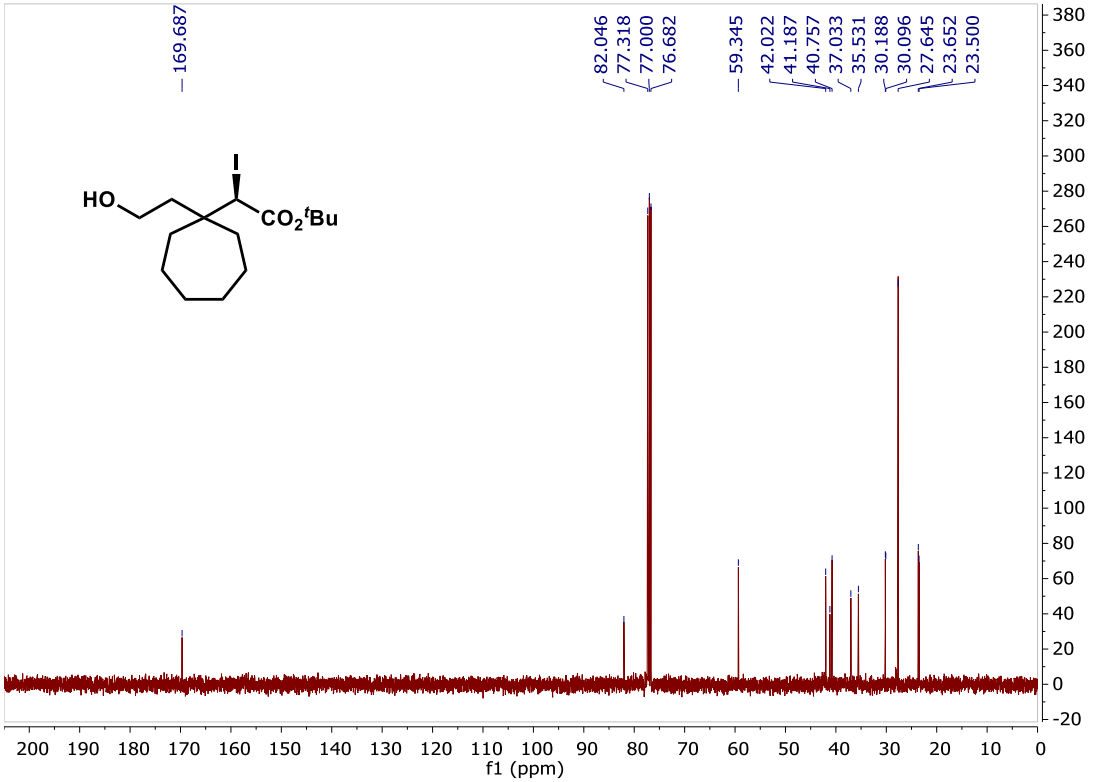
(+)-*tert*-Butyl (*R*)-5-hydroxy-2-iodo-3,3-dimethylpentanoate, 6s



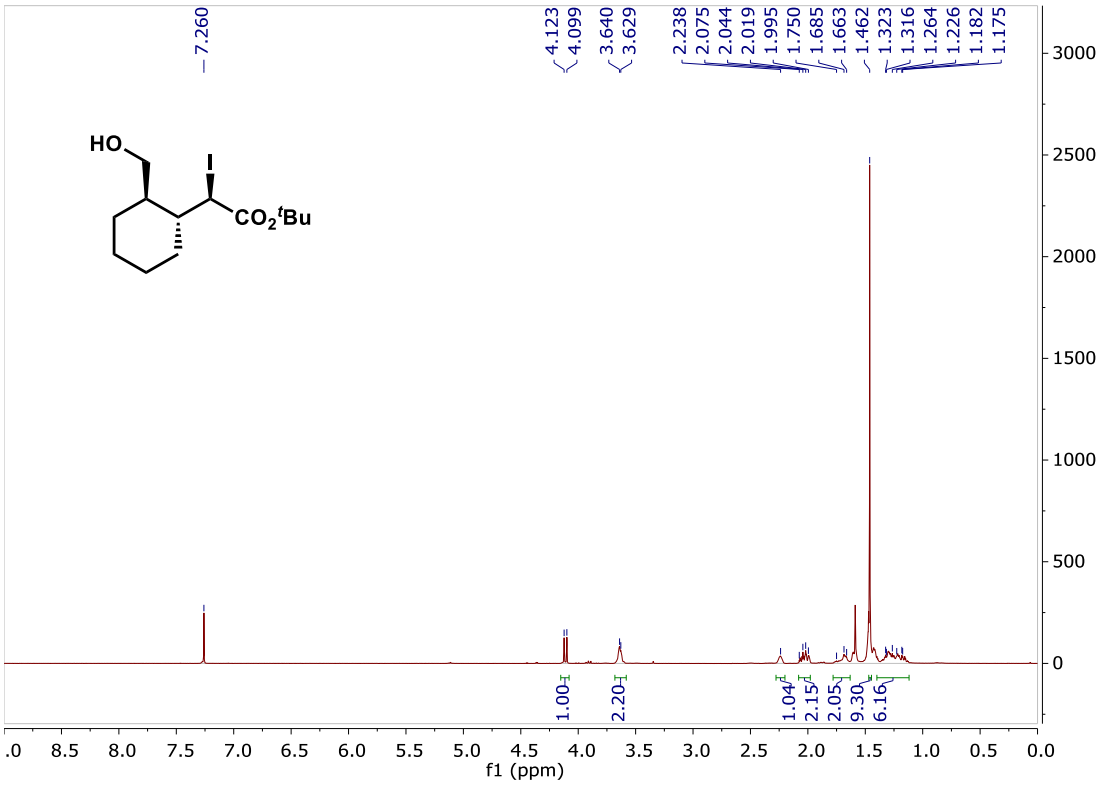


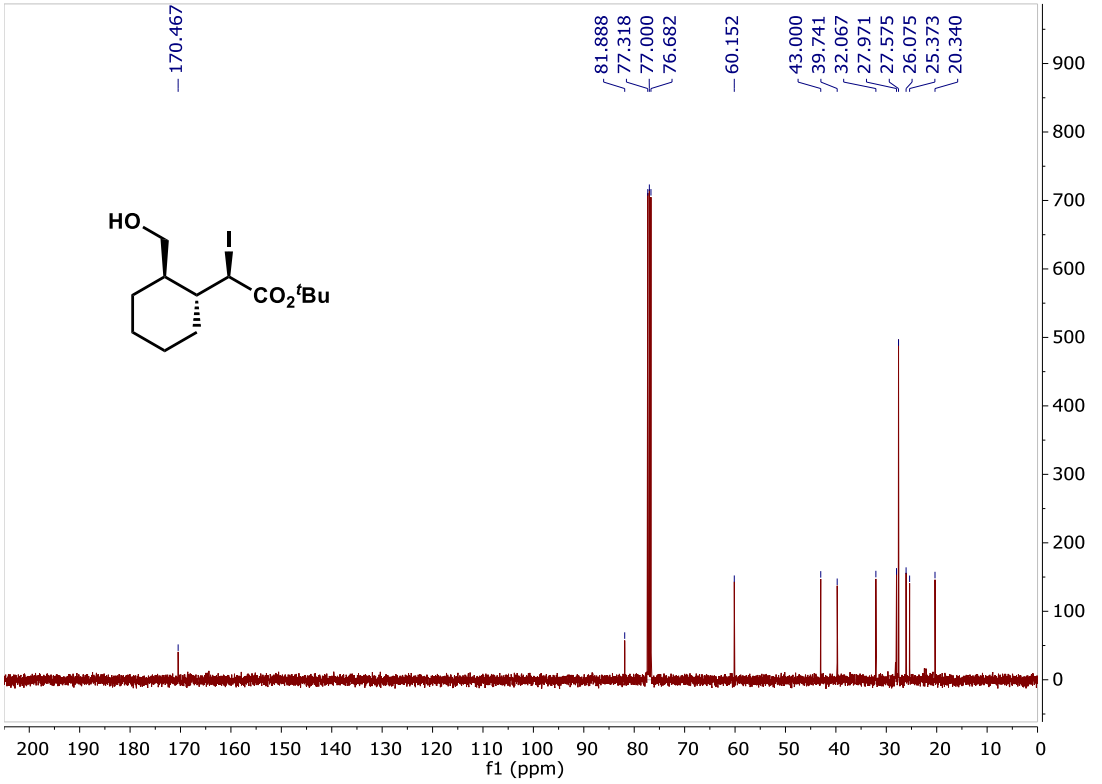
(+)-*tert*-Butyl (*R*)-2-(1-(2-hydroxyethyl)cycloheptyl)-2-iodoacetate, 6v



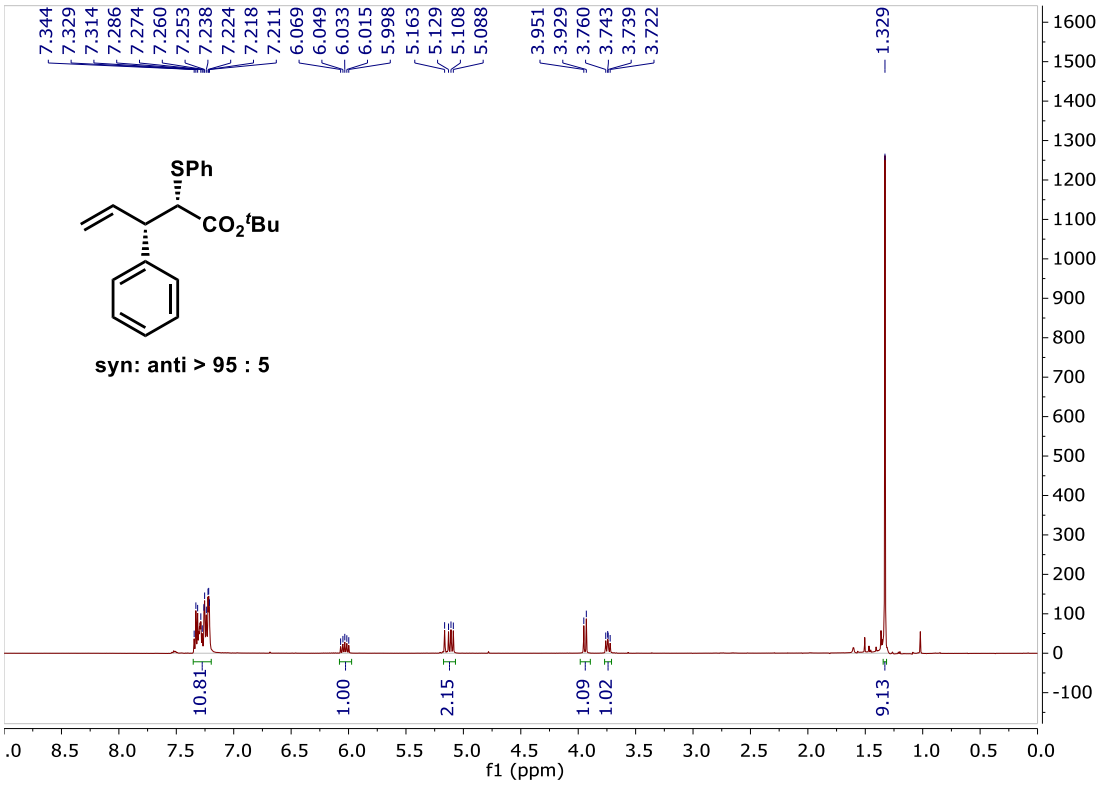


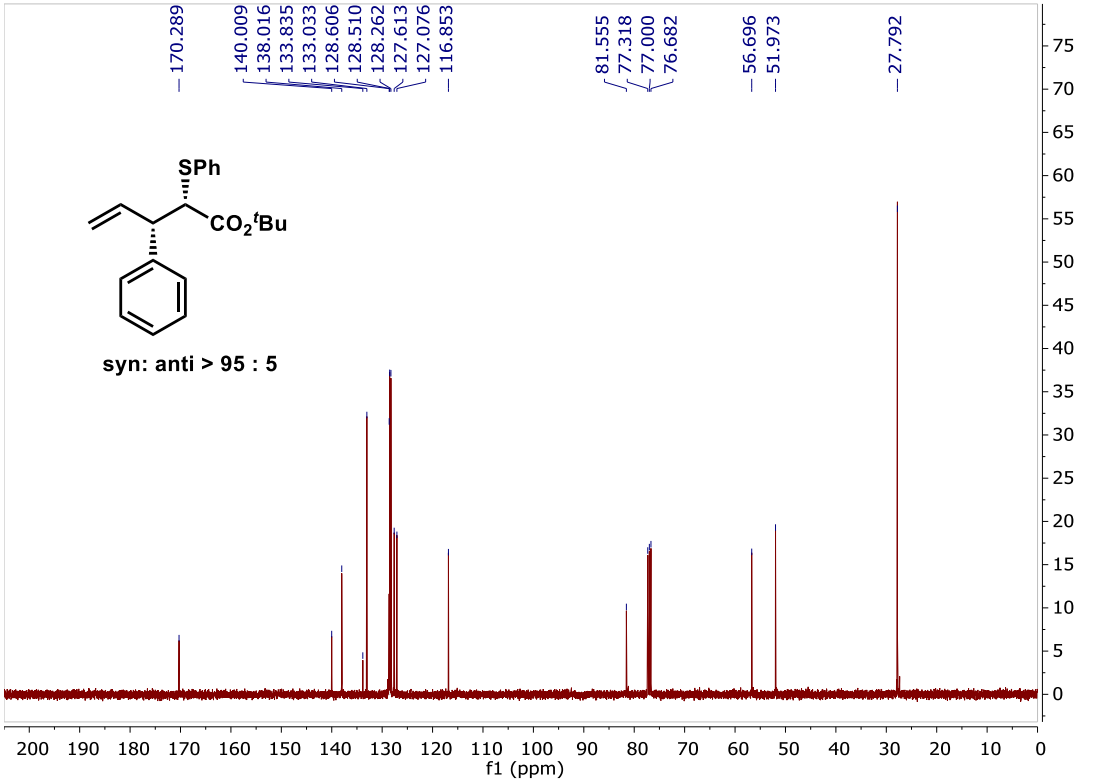
(+)-*tert*-Butyl (2*R*)-2-((1*R*)-2-(hydroxymethyl)cyclohexyl)-2-iodoacetate, 6y



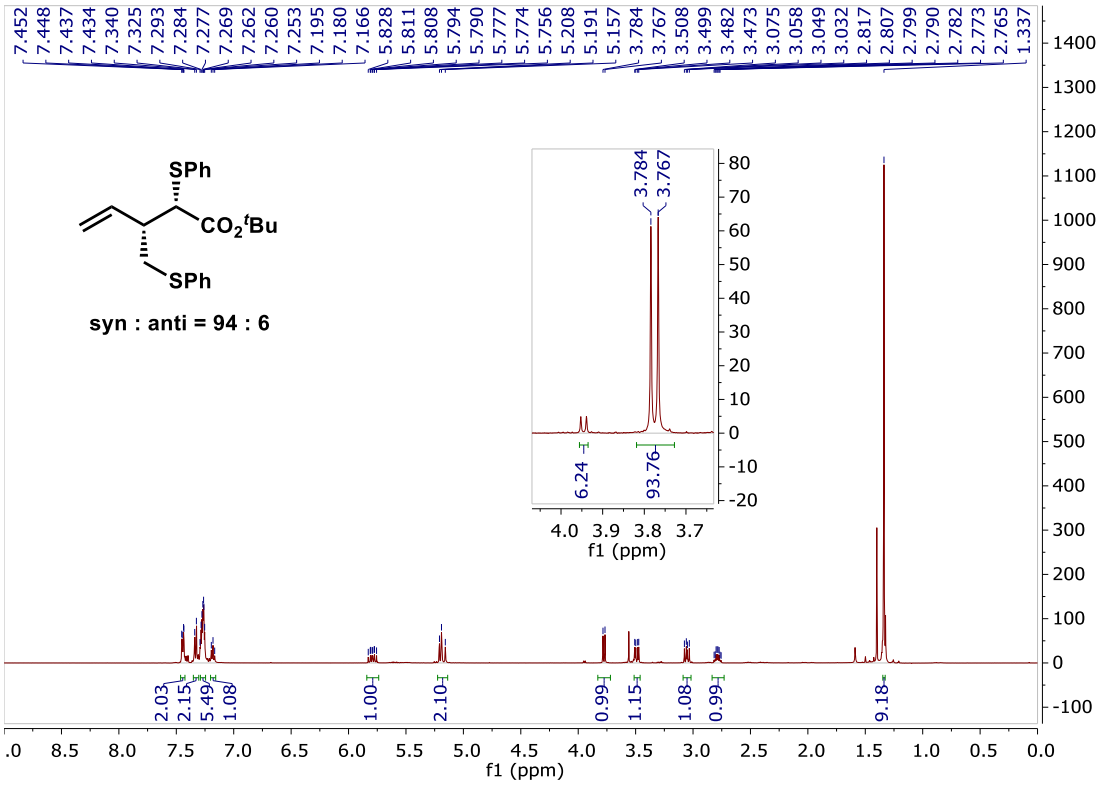


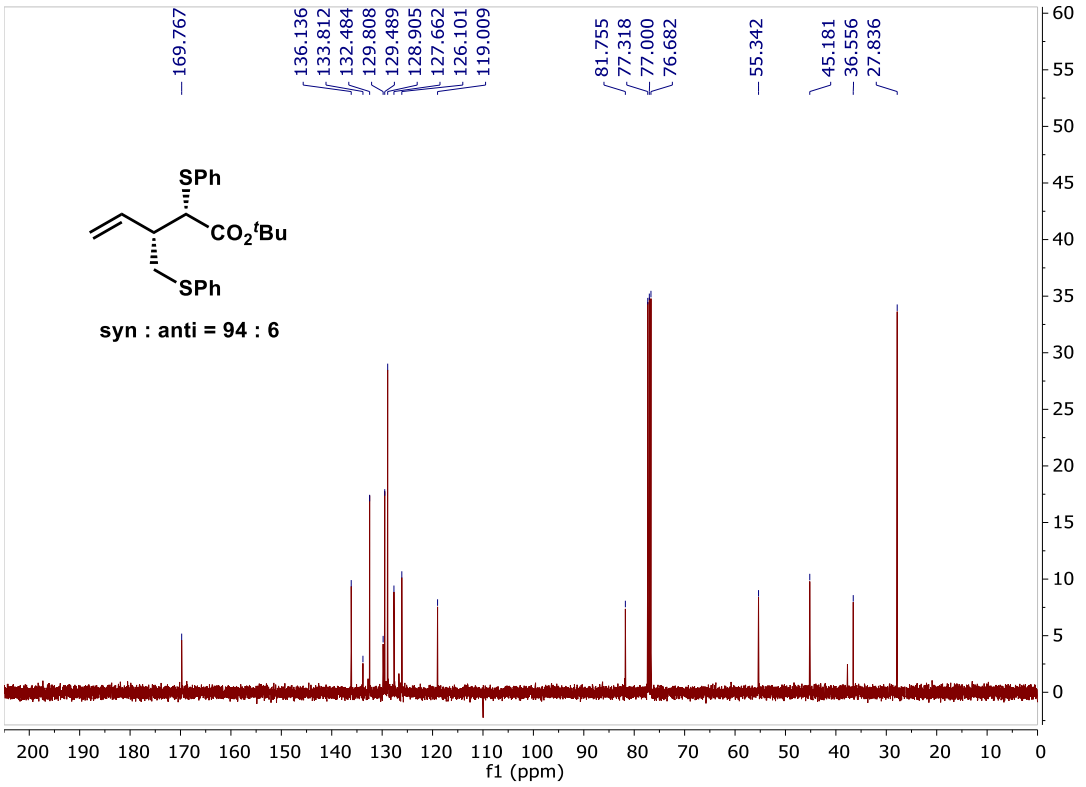
(–)-*tert*-Butyl (2*S*, 3*S*)-3-phenyl-2-(phenylthio)pent-4-enoate, 7a



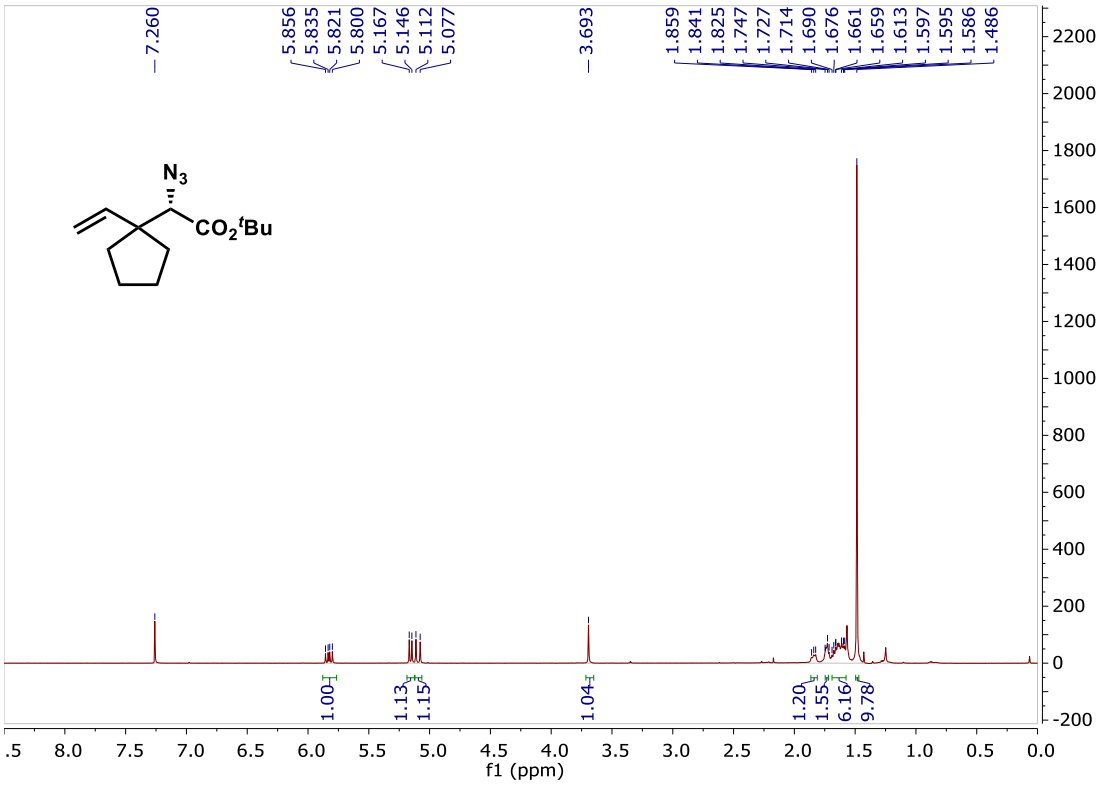


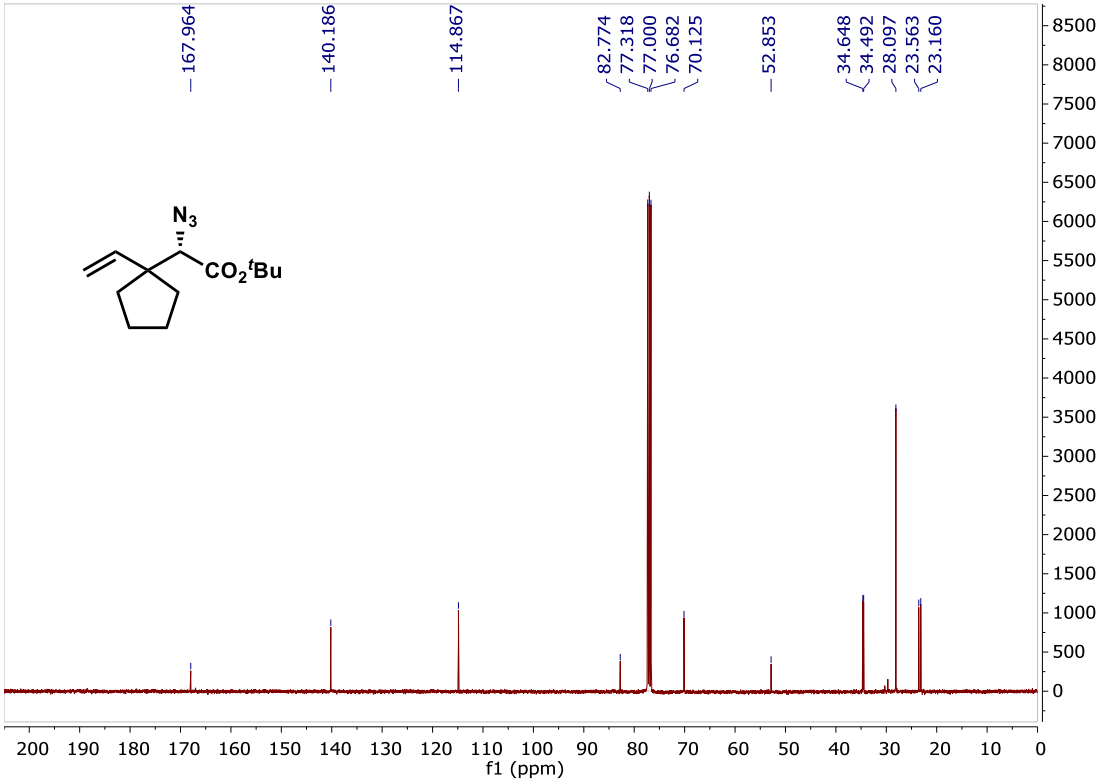
(–)-*tert*-Butyl (2*S*, 3*S*)-2-(phenylthio)-3-((phenylthio)methyl)pent-4-enoate, 7q



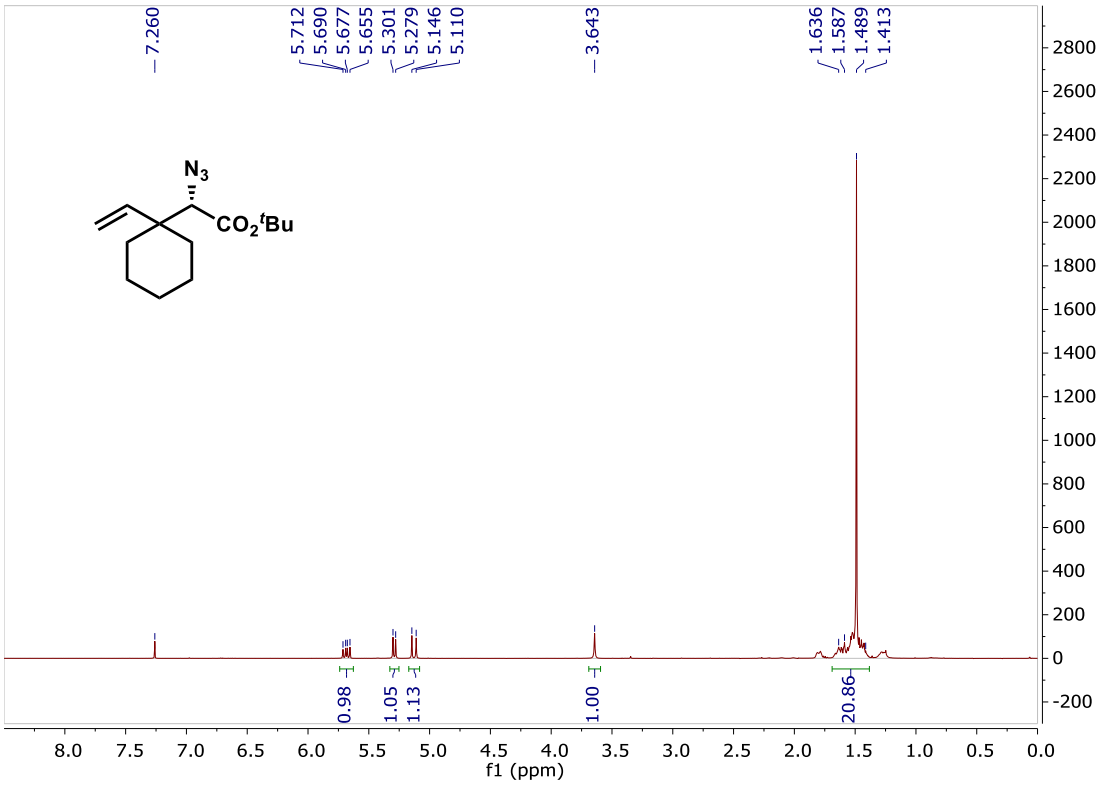


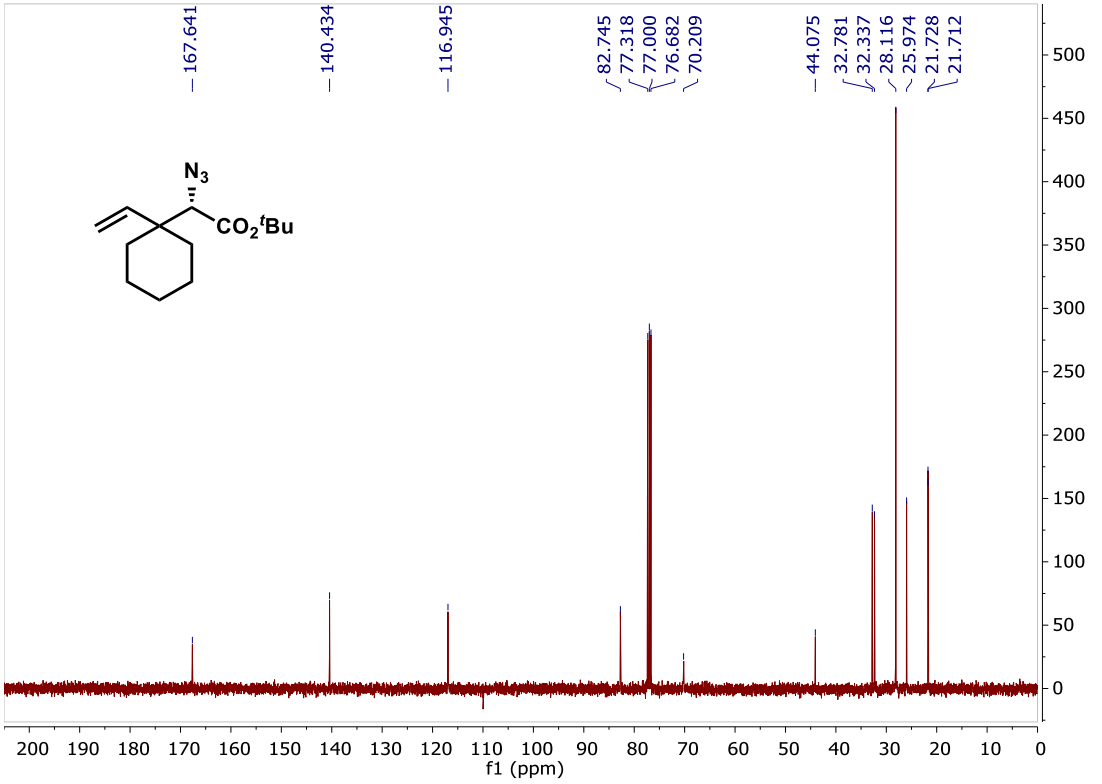
(–)-*tert*-Butyl (*S*)-2-azido-2-(1-vinylcyclopentyl)acetate, 8t



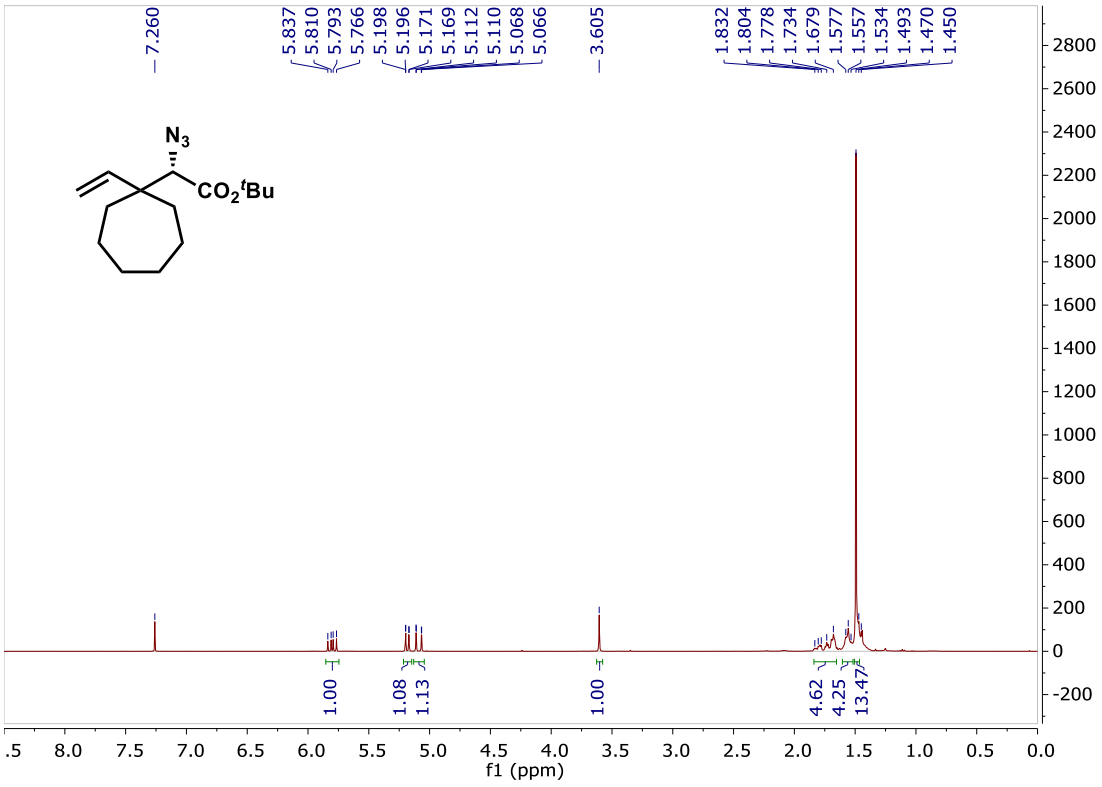


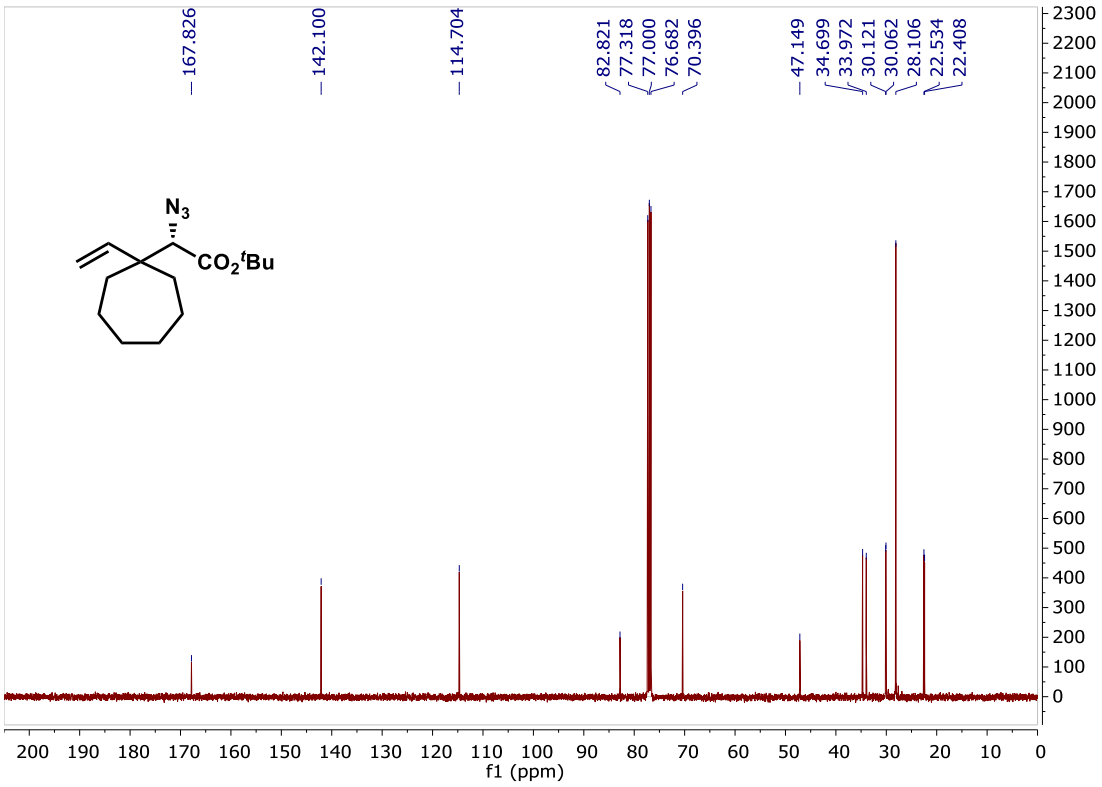
(–)-tert-Butyl (*S*)-2-azido-2-(1-vinylcyclohexyl)acetate, 8u



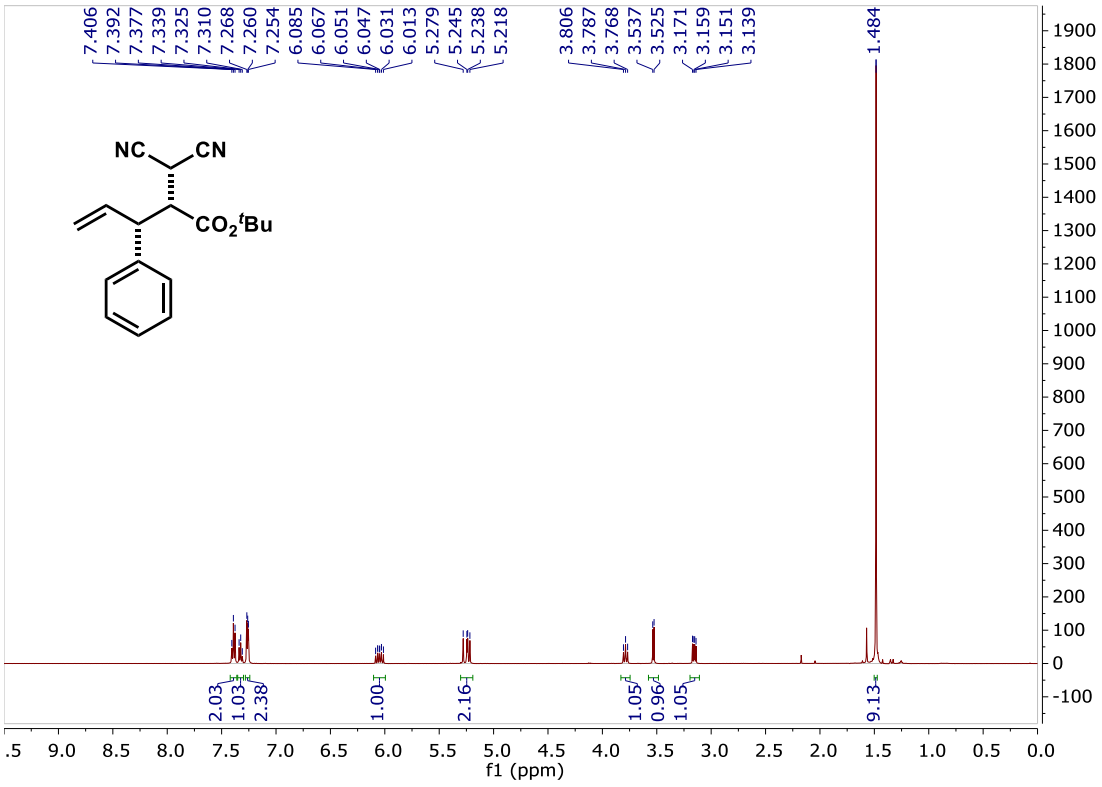


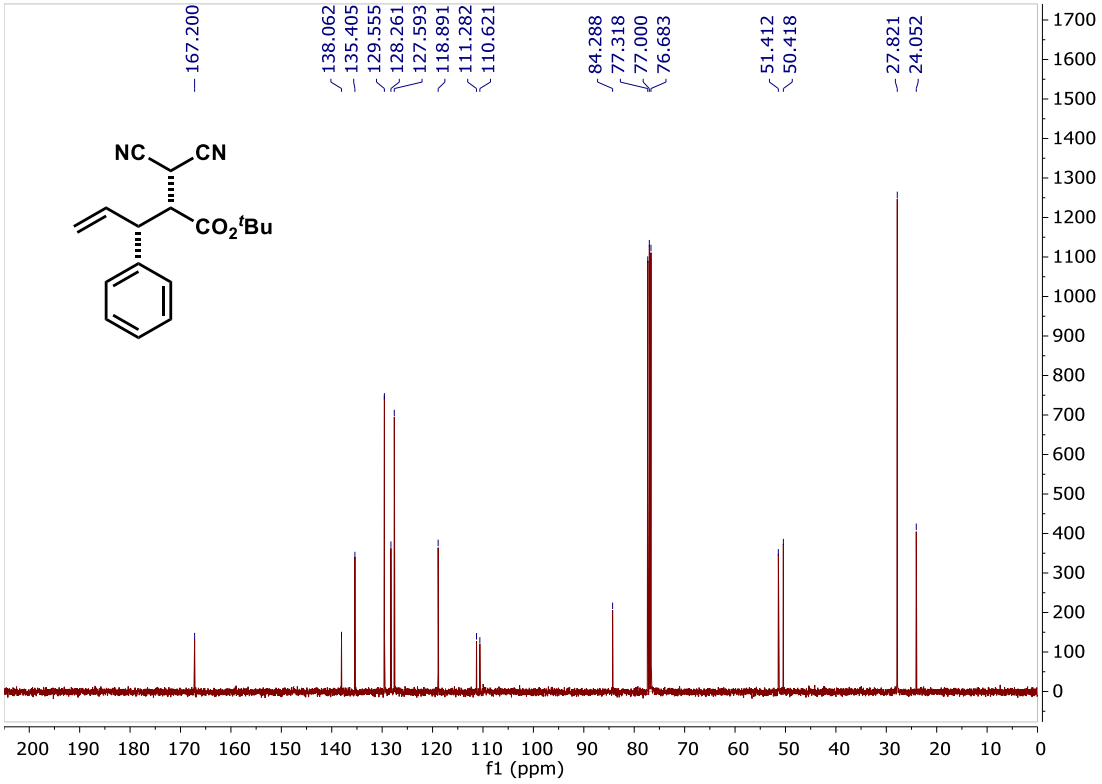
(–)-*tert*-Butyl (*S*)-2-azido-2-(1-vinylcycloheptyl)acetate, 8v



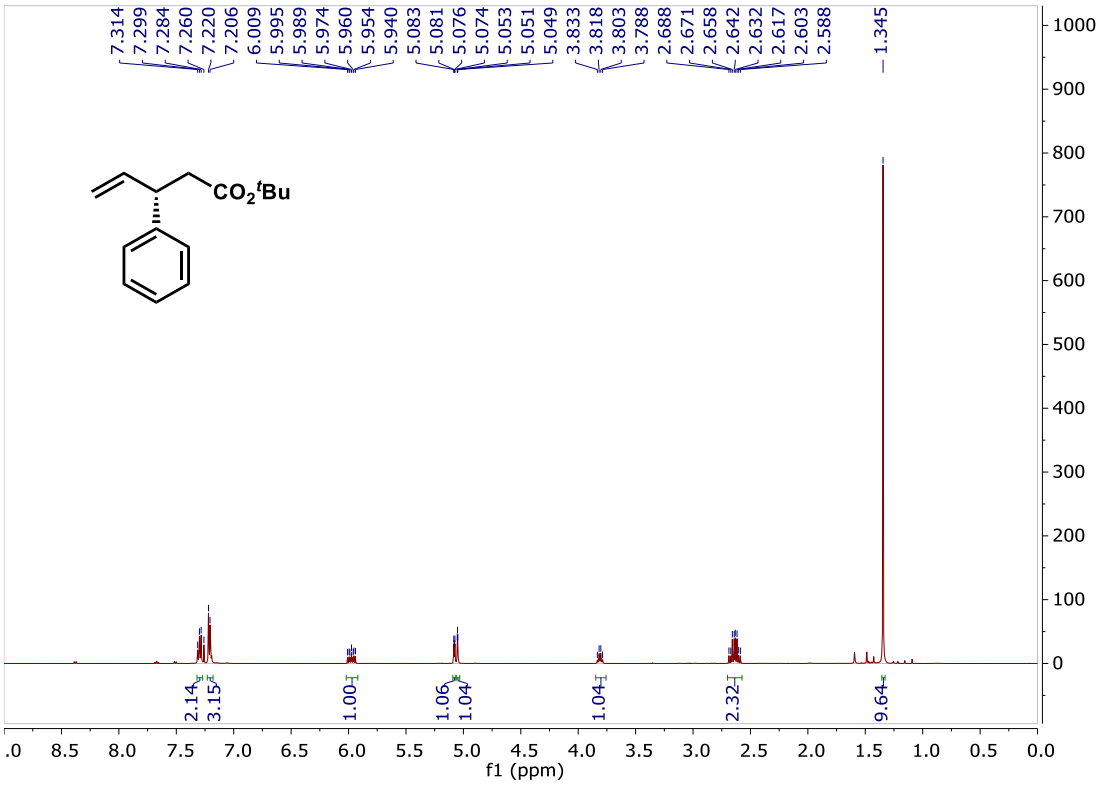


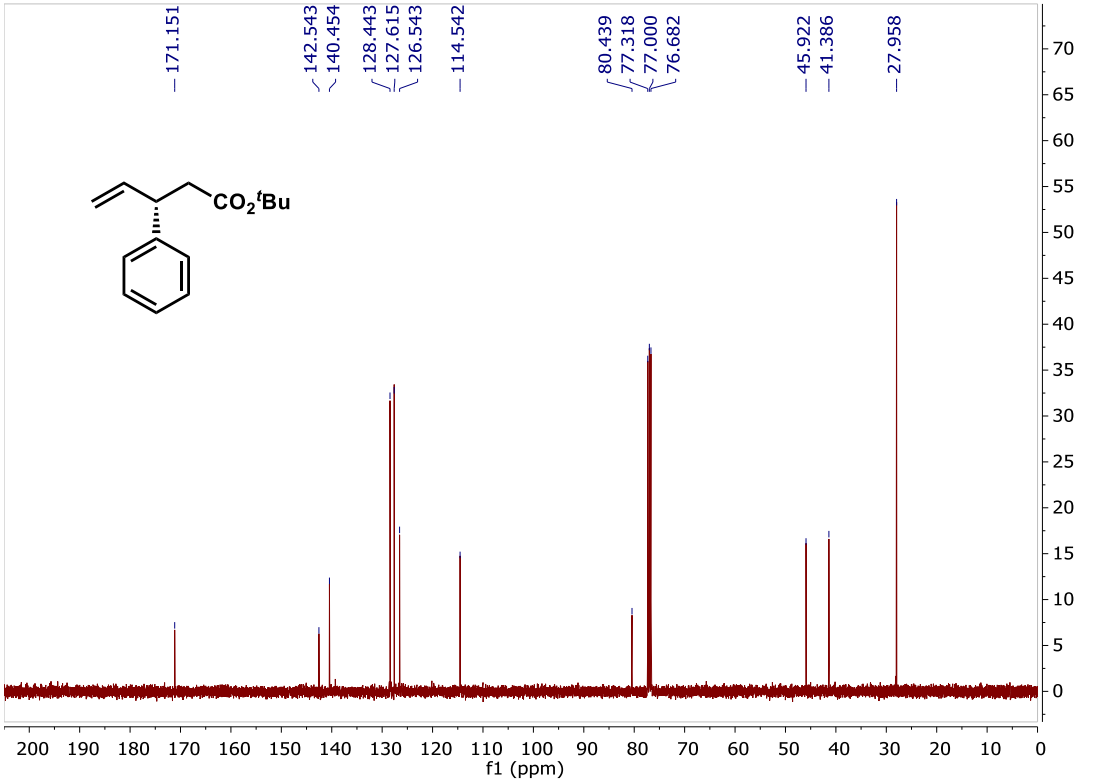
(+)-*tert*-Butyl (2*R*, 3*R*)-2-(dicyanomethyl)-3-phenylpent-4-enoate, 9a



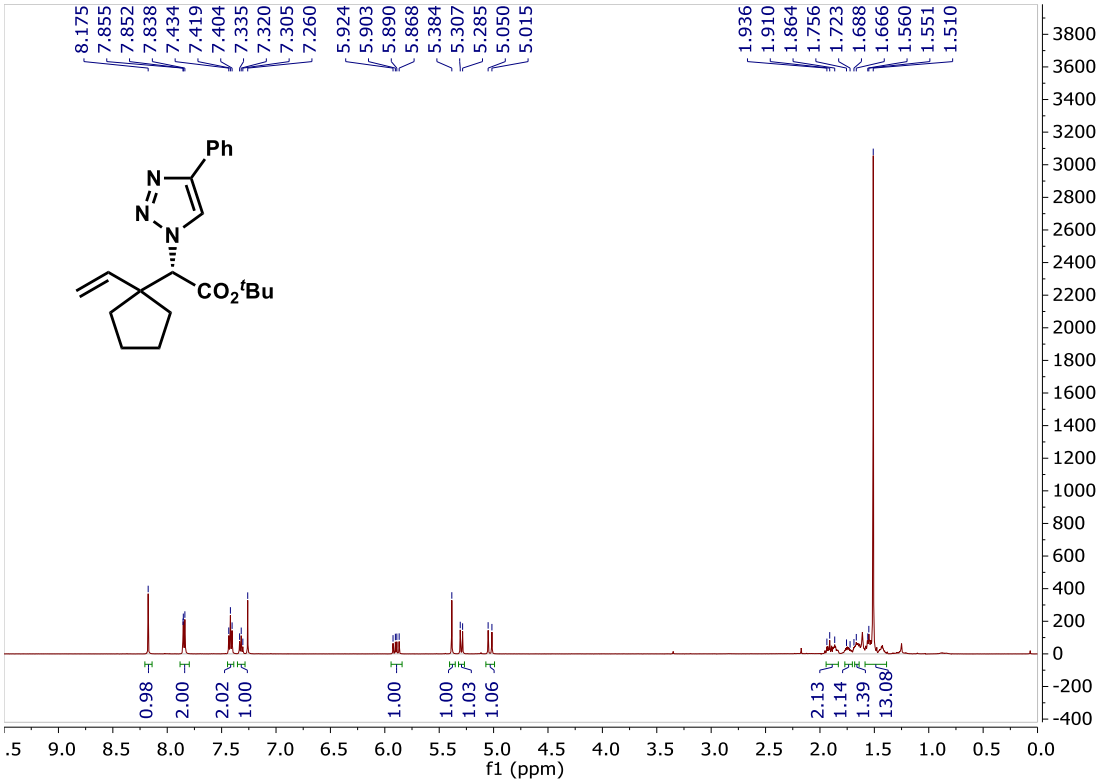


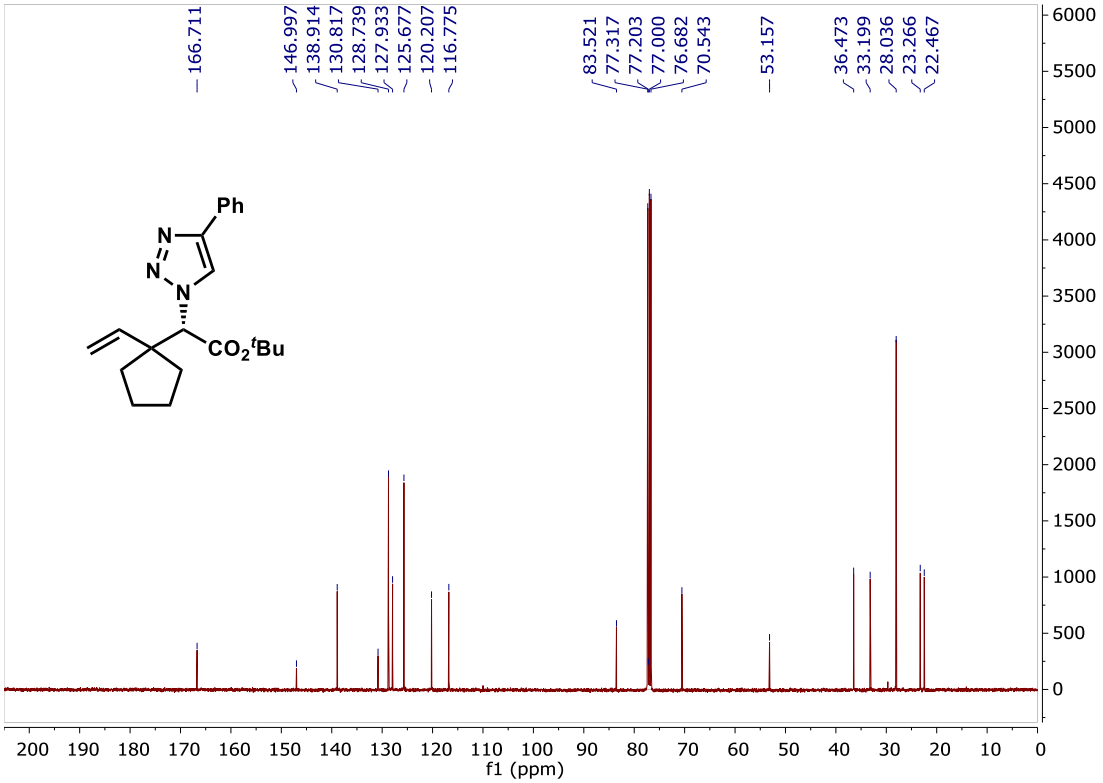
(+)-*tert*-Butyl (*S*)-3-phenylpent-4-enoate, 10a



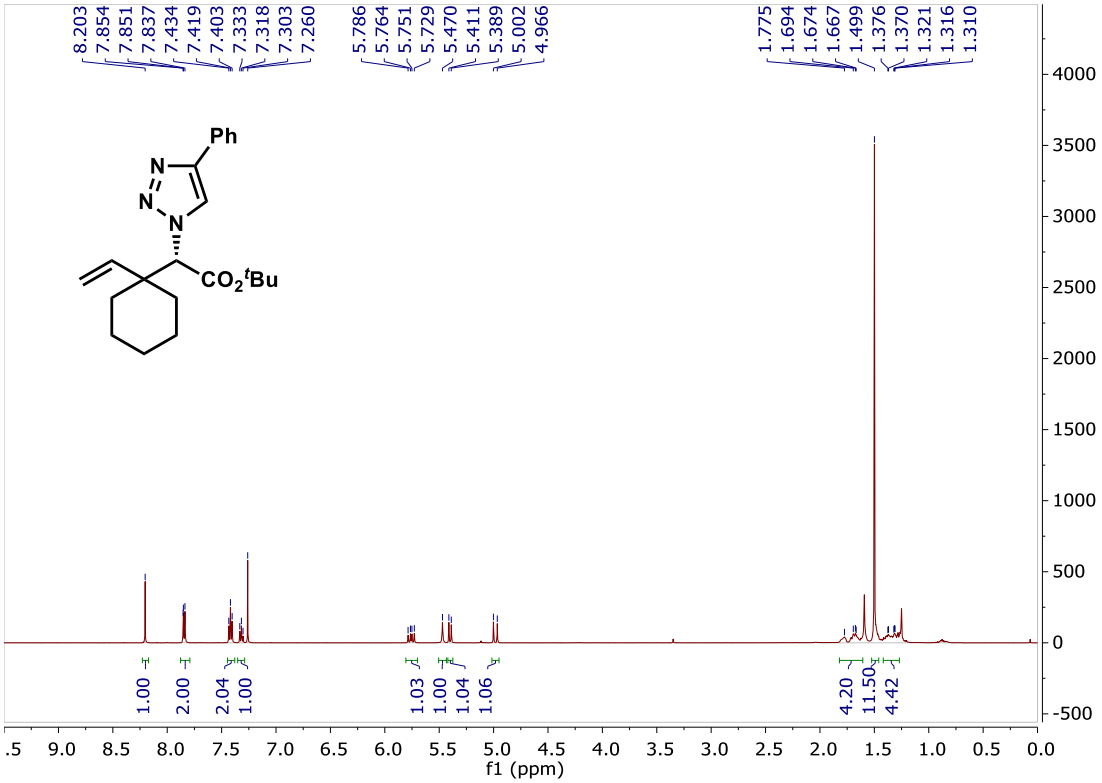


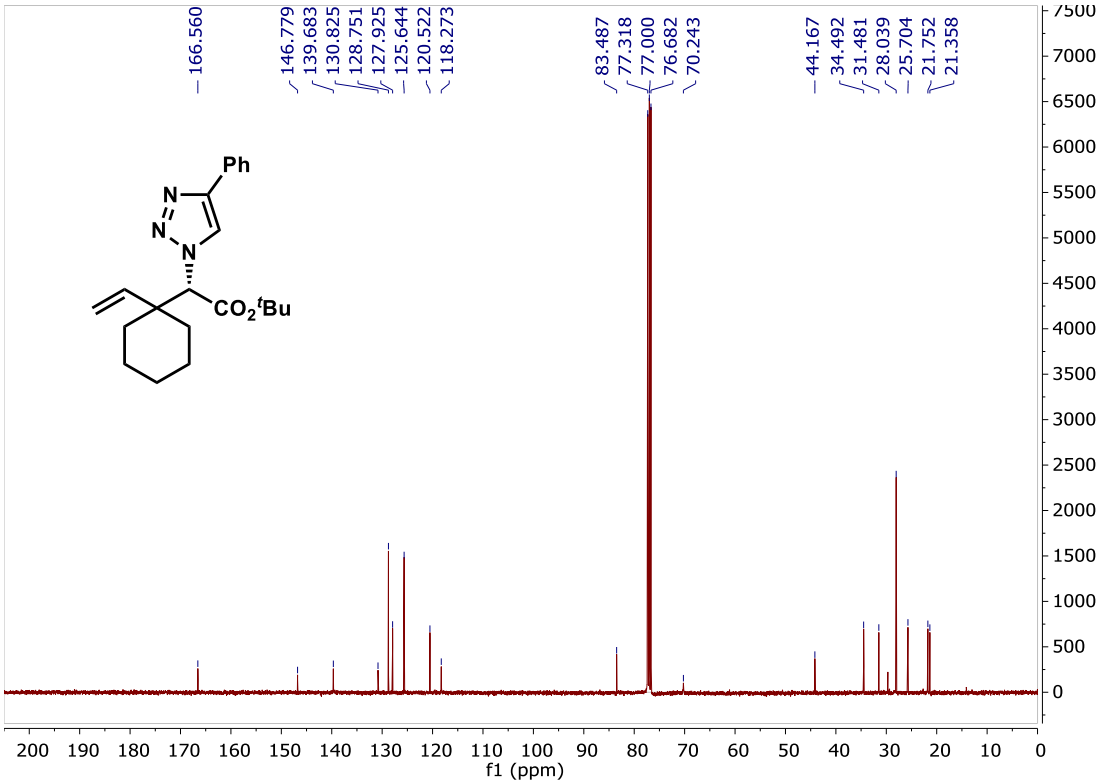
(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcyclopentyl)acetate, S11t



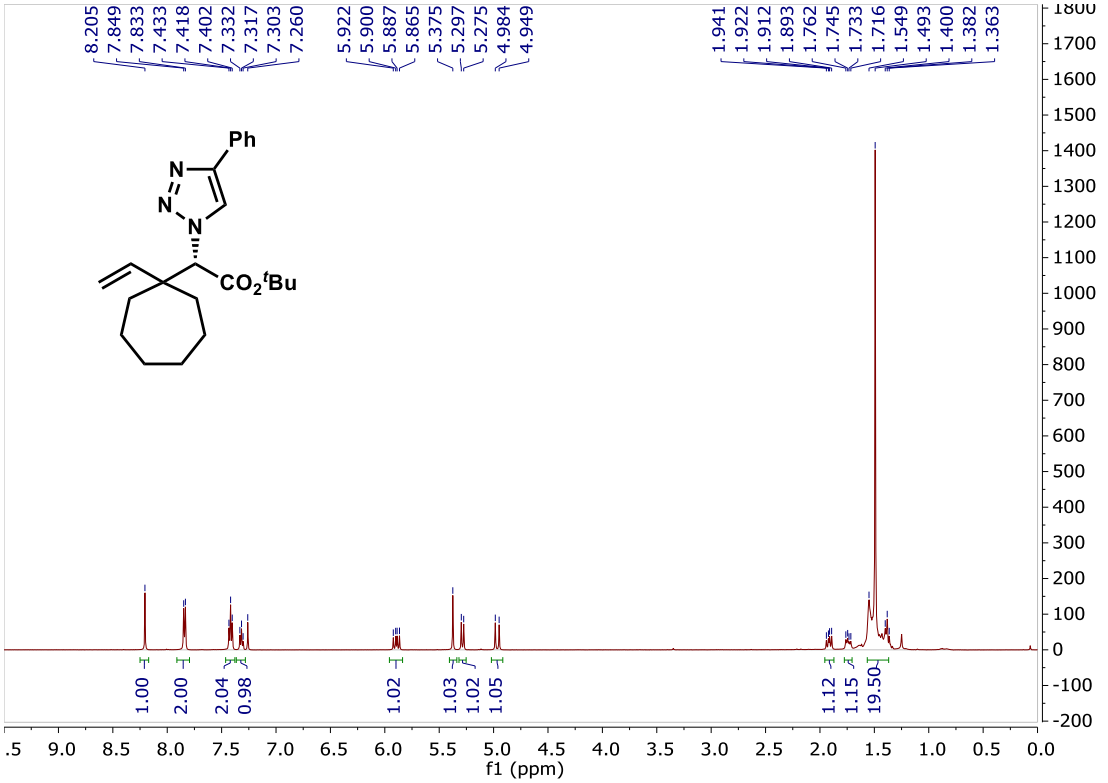


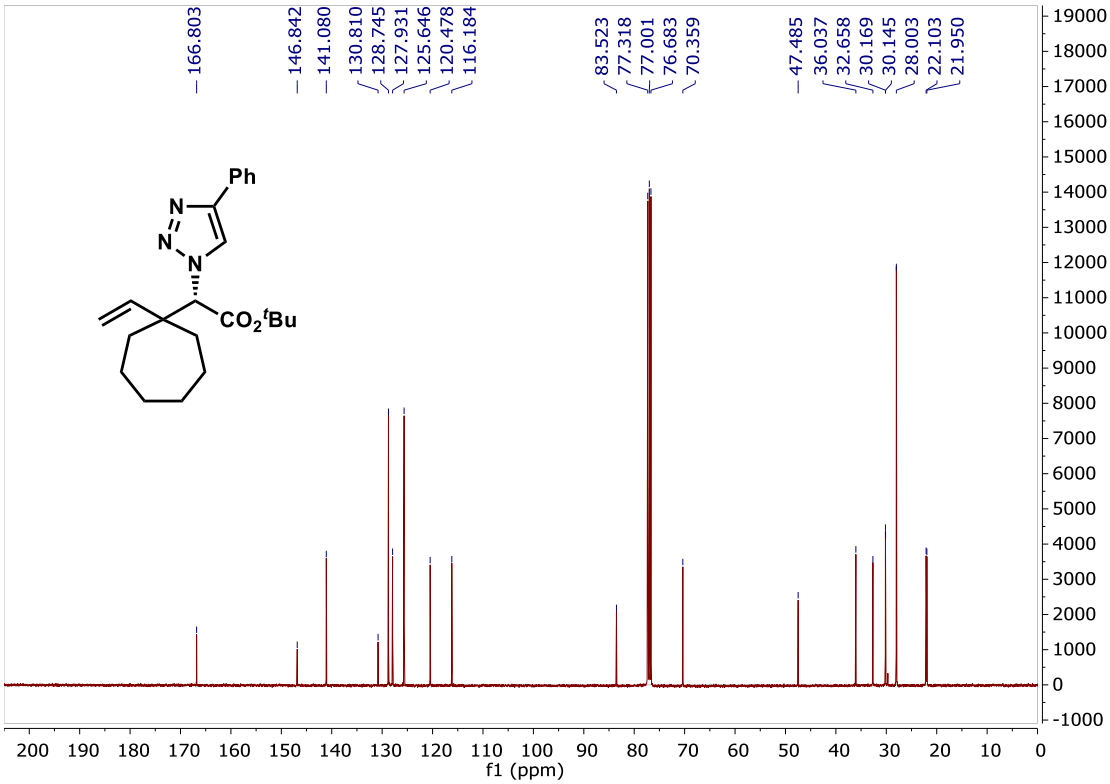
(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcyclohexyl)acetate, S11u





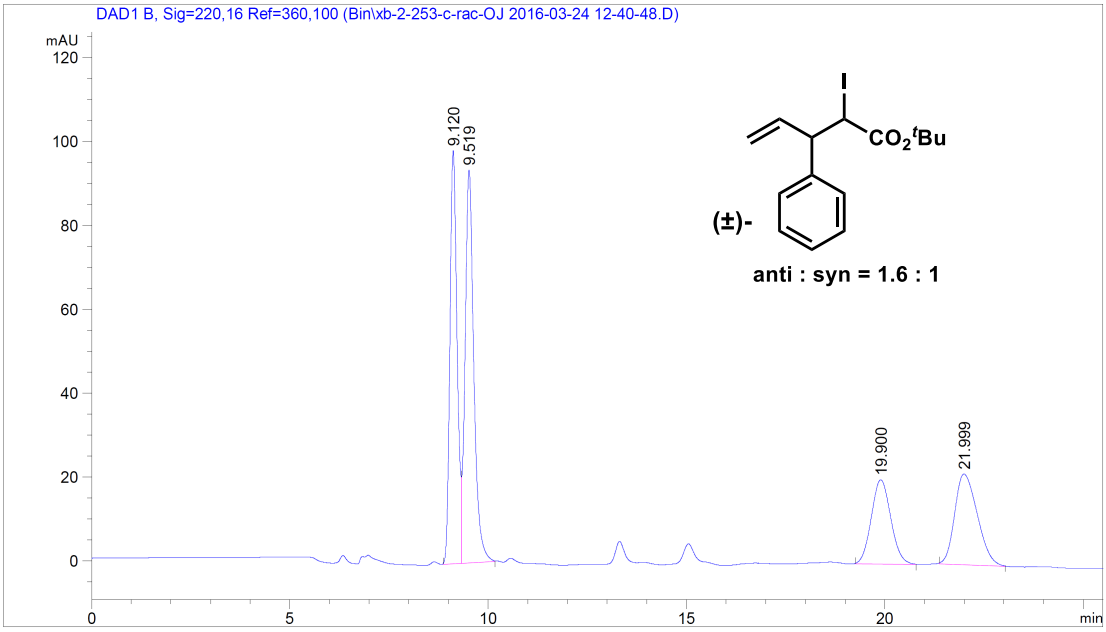
(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcycloheptyl)acetate, S11v



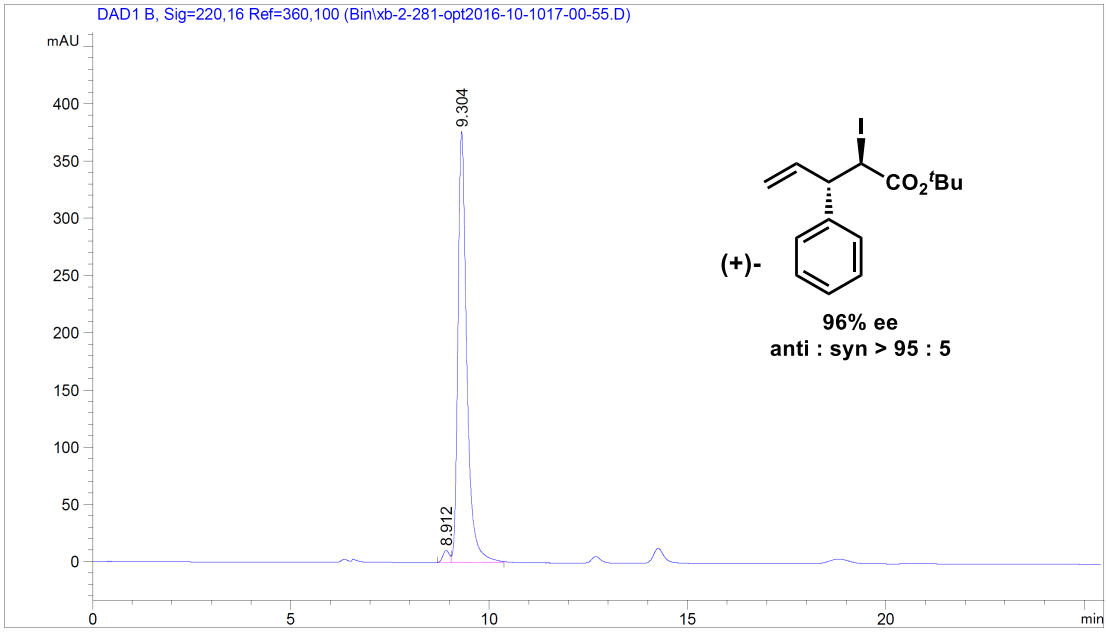


12. HPLC Charts

(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-phenylpent-4-enoate, 5a

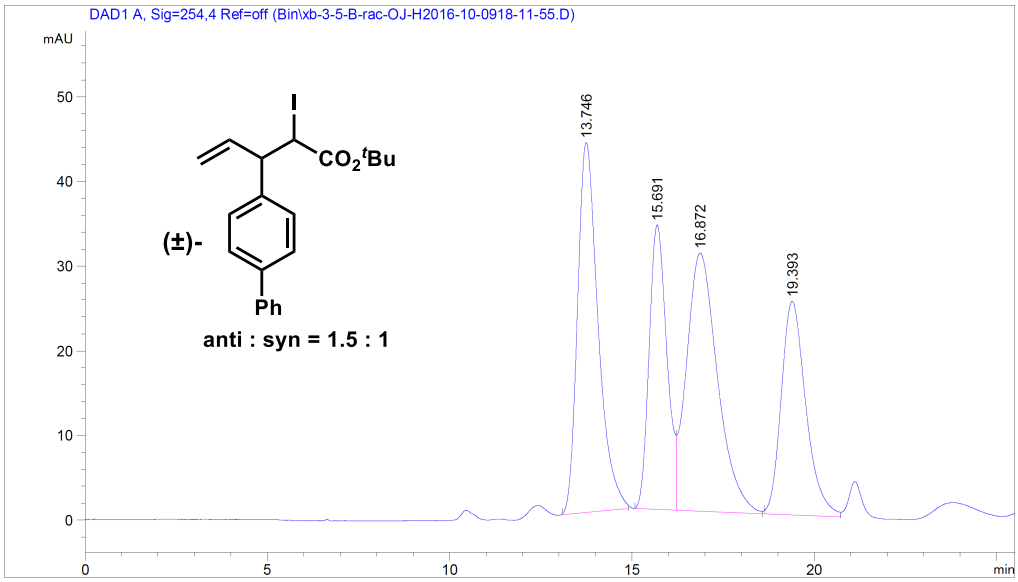


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	9.120	BV	0.1920	1241.80640	29.4126	?
2	9.519	VB	0.2289	1438.31628	34.0670	?
3	19.900	BB	0.5205	684.29065	16.2076	?
4	21.999	BB	0.6163	857.61230	20.3128	?

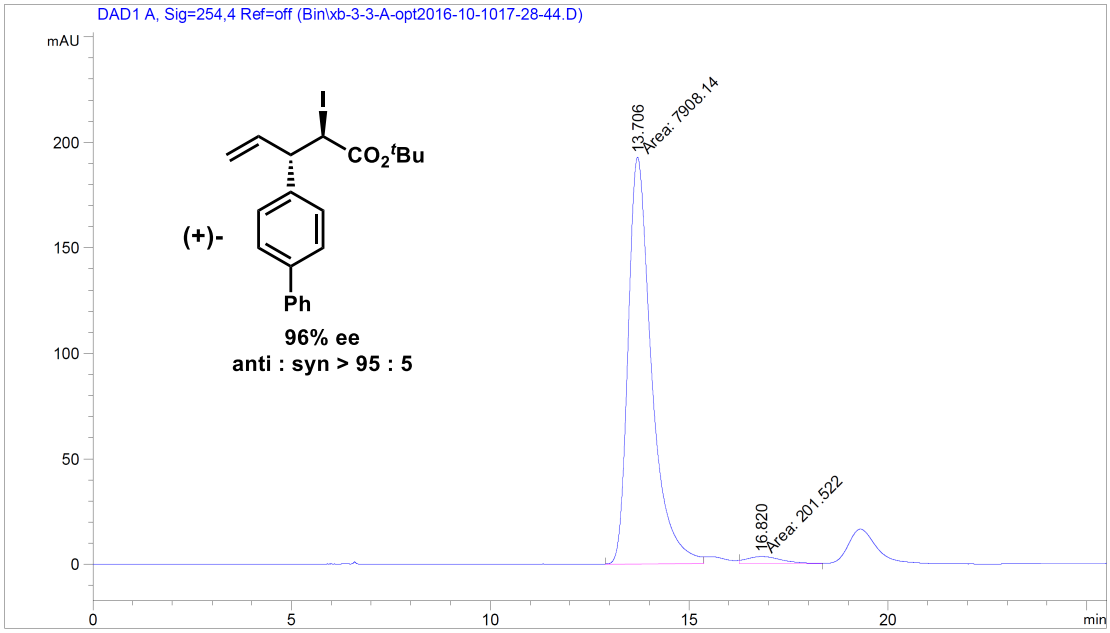


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	8.912	BV	0.1746	118.39743	1.9901	?
2	9.304	VB	0.2317	5830.78418	98.0099	?

(+)-*tert*-Butyl (2*R*, 3*S*)-3-([1,1'-biphenyl]-4-yl)-2-iodopent-4-enoate, 5b

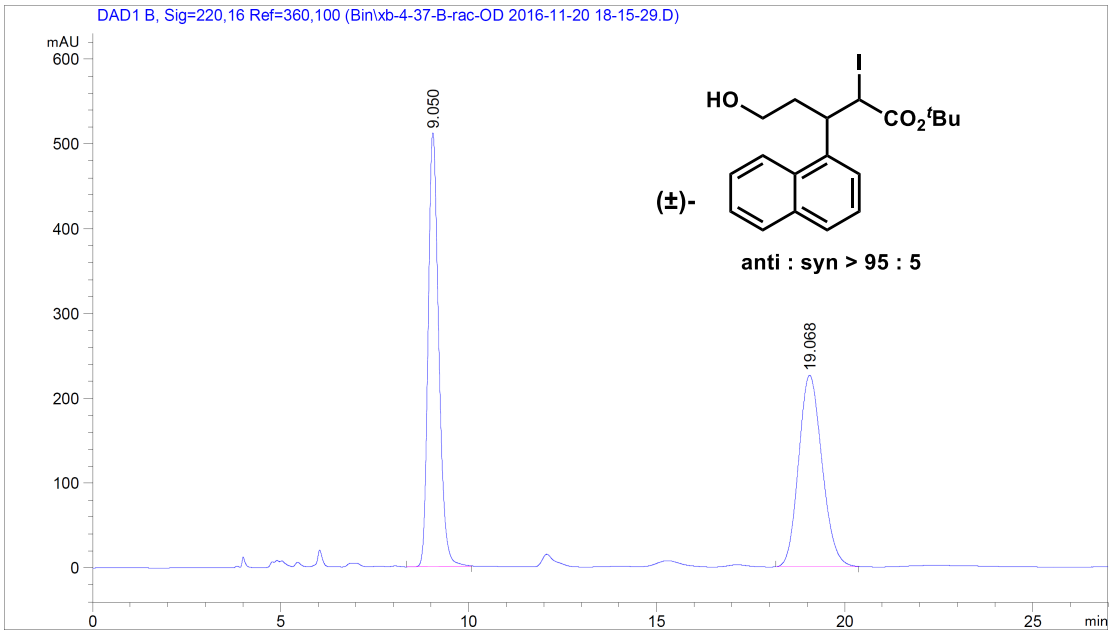


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	13.746	BB	0.5793	1713.08752	29.3263	?
2	15.691	BV	0.5155	1135.77490	19.4433	?
3	16.872	VB	0.7725	1805.15479	30.9024	?
4	19.393	BV	0.6823	1187.45190	20.3280	?

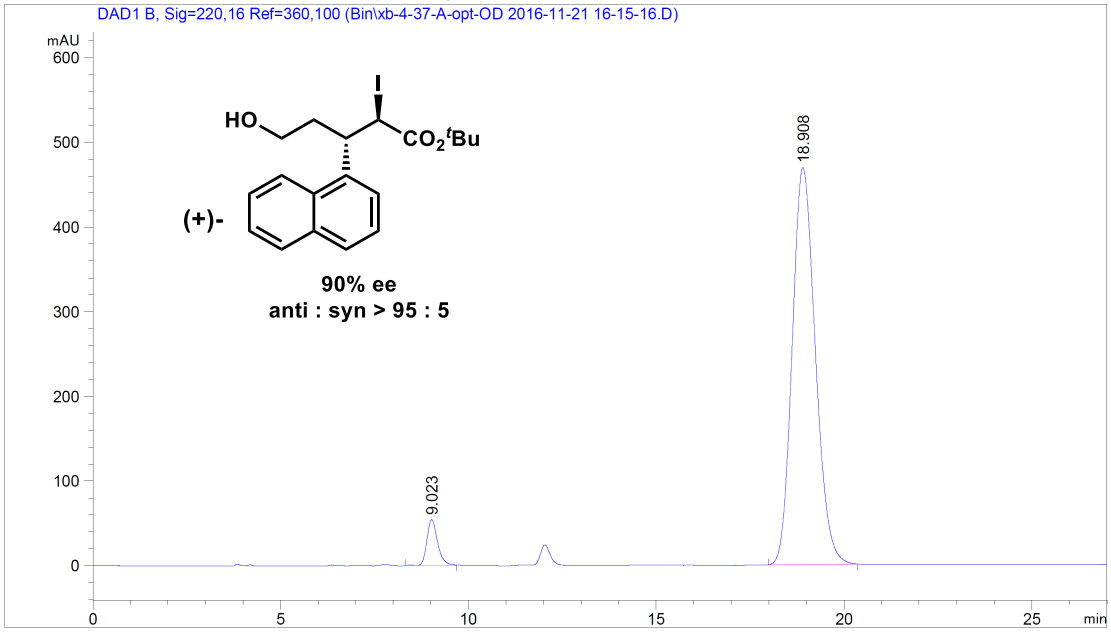


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	13.706	MM	0.6837	7908.13623	97.5150	?
2	16.820	MM	1.0066	201.52228	2.4850	?

(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(naphthalen-1-yl)pentanoate, 6c

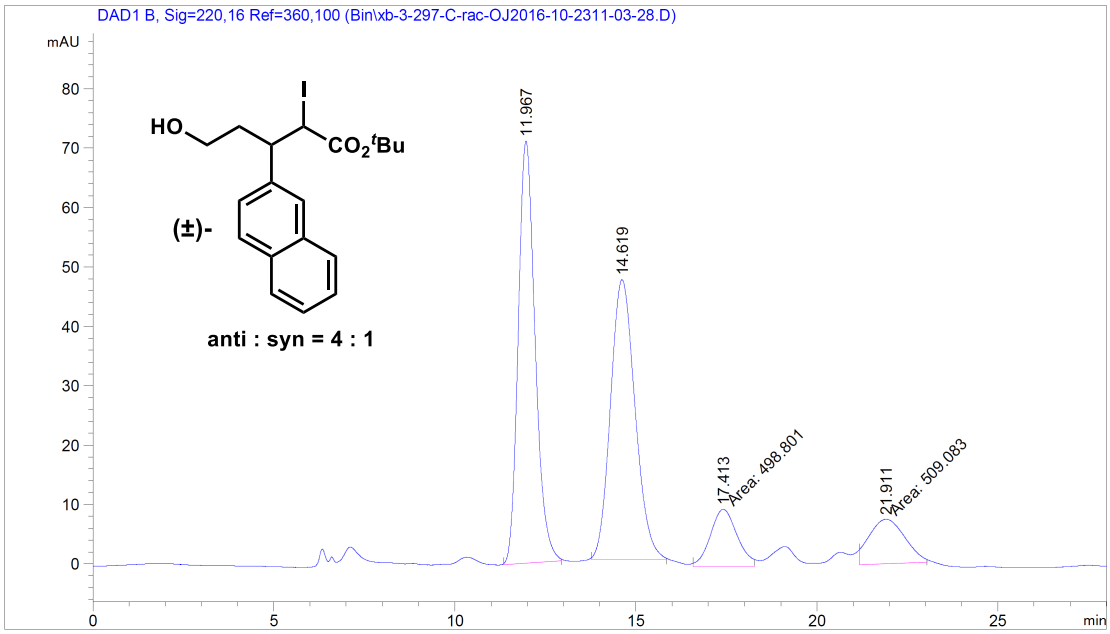


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.050	VB	0.3010	1.00012e4	50.4950
2	19.068	BB	0.6731	9805.08105	49.5050

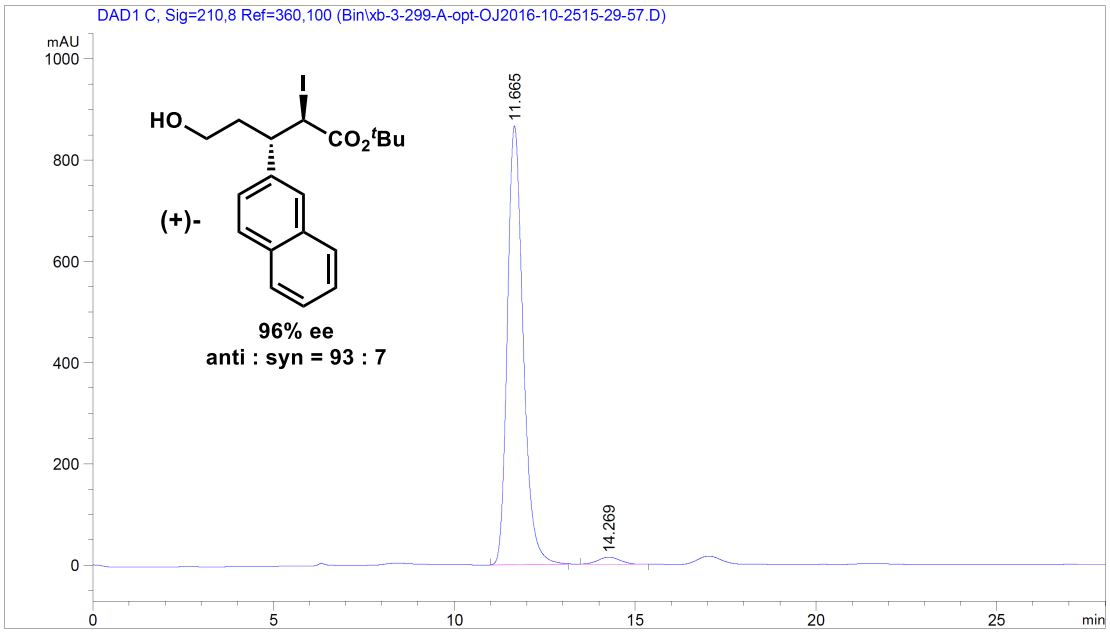


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.023	BB	0.3050	1084.06201	5.1268
2	18.908	BB	0.6650	2.00610e4	94.8732

(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(naphthalen-2-yl)pentanoate, 6d

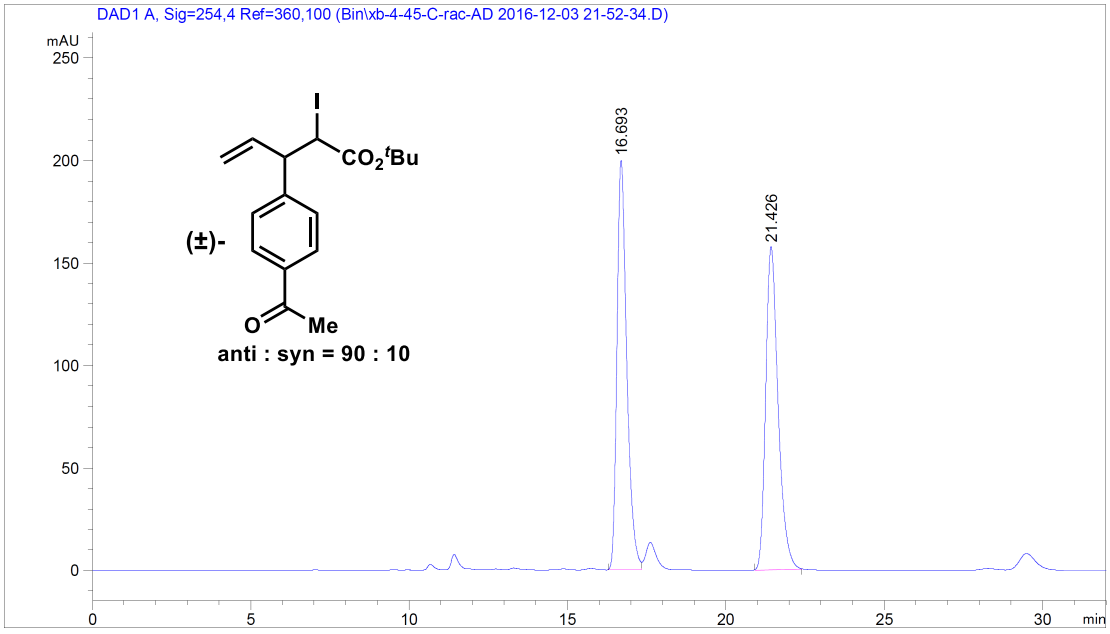


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	11.967	BB	0.4966	2298.86743	41.5474	?
2	14.619	BB	0.7088	2226.37305	40.2372	?
3	17.413	MM	0.8573	498.80063	9.0148	?
4	21.911	MM	1.1362	509.08344	9.2007	?

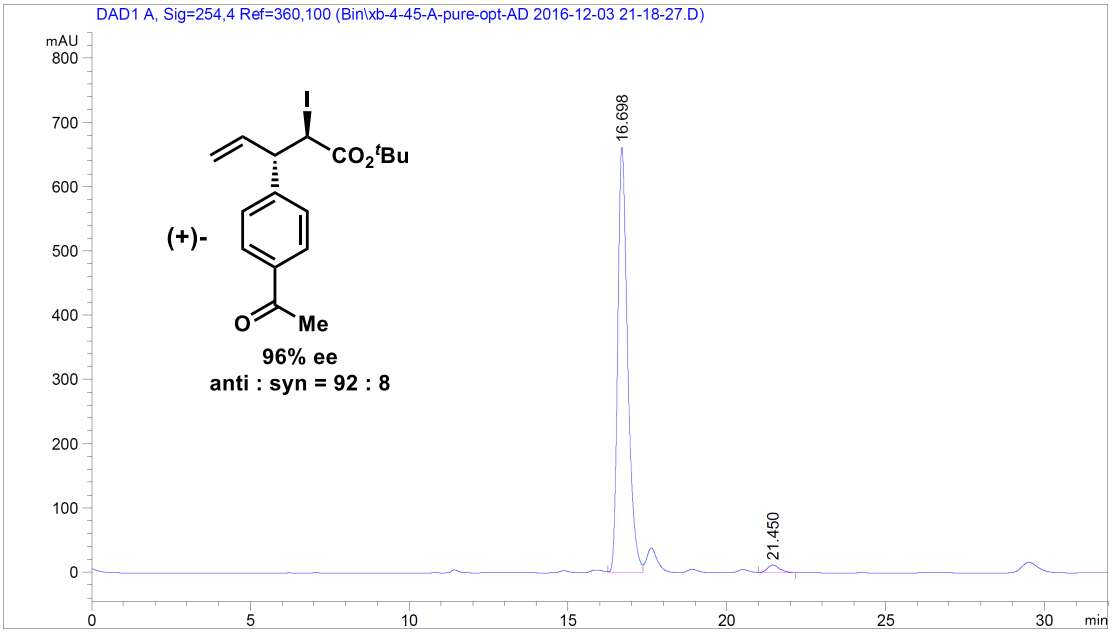


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	11.665	BB	0.4678	2.62922e4	97.8991	?
2	14.269	BB	0.5571	564.23779	2.1009	?

(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-acetylphenyl)-2-iodopent-4-enoate, 5e

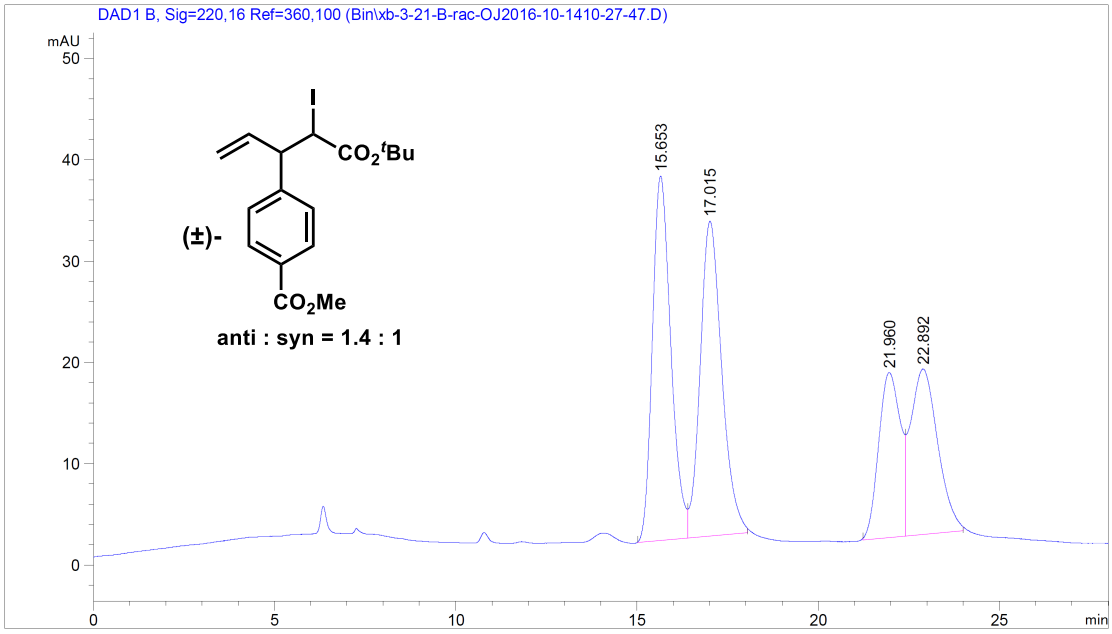


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	16.693	BV	0.3268	4314.40137	50.0348
2	21.426	BB	0.4118	4308.40332	49.9652

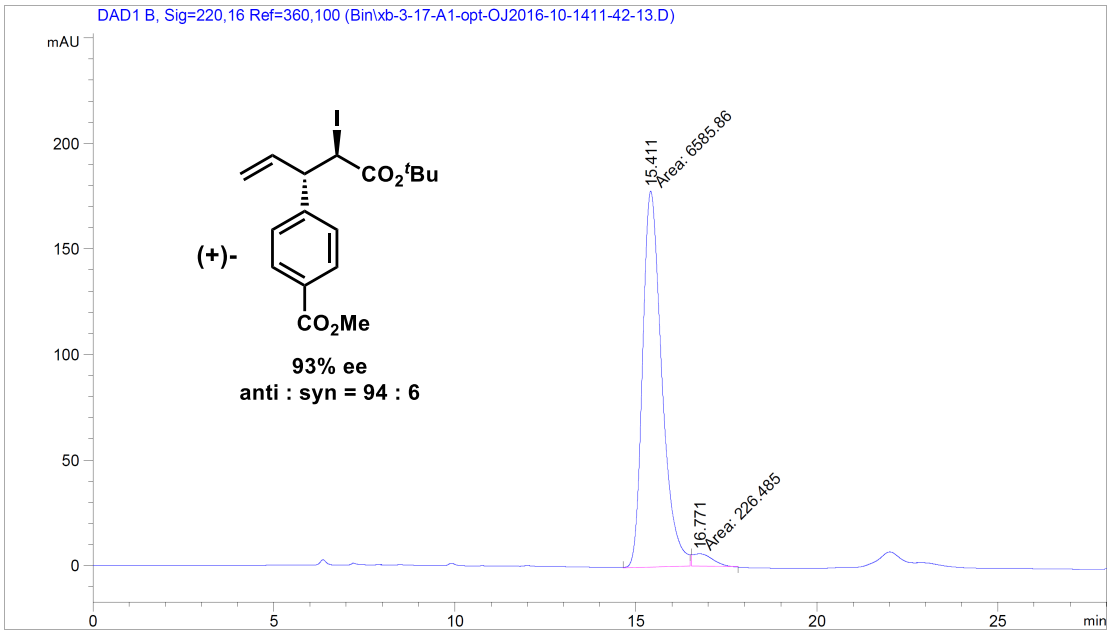


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	16.698	VV	0.3303	1.44331e4	97.8395
2	21.450	VB	0.3914	318.70676	2.1605

(+)-Methyl 4-((3*S*, 4*R*)-5-(*tert*-butoxy)-4-iodo-5-oxopent-1-en-3-yl)benzoate, 5f

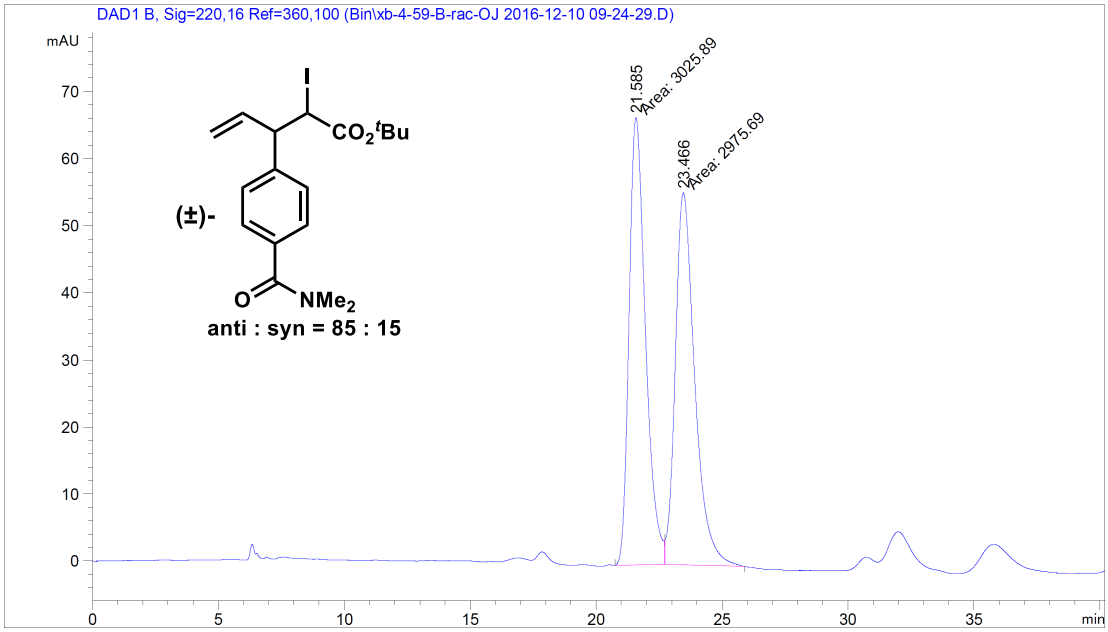


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	15.653	BV	0.5323	1271.77173	31.1124	?
2	17.015	VB	0.6315	1287.41833	31.4952	?
3	21.960	BV	0.6105	679.67938	16.6276	?
4	22.892	VB	0.7389	848.79938	20.7649	?

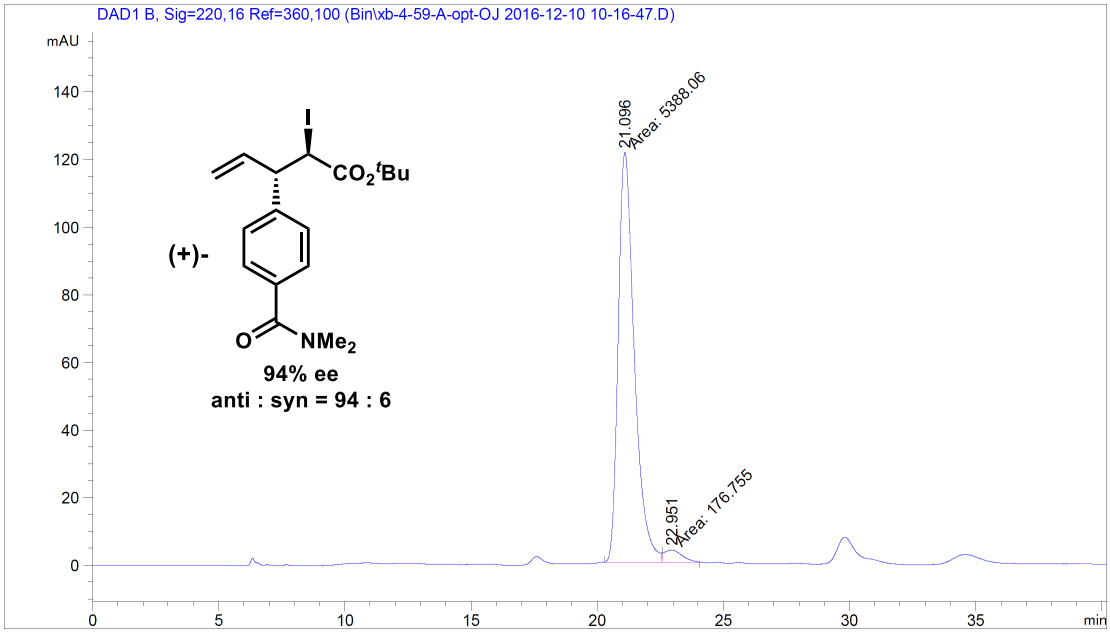


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	15.411	MM	0.6161	6585.86328	96.6754	?
2	16.771	MM	0.6374	226.48479	3.3246	?

(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-(dimethylcarbamoyl)phenyl)-2-iodopent-4-enoate, 5g

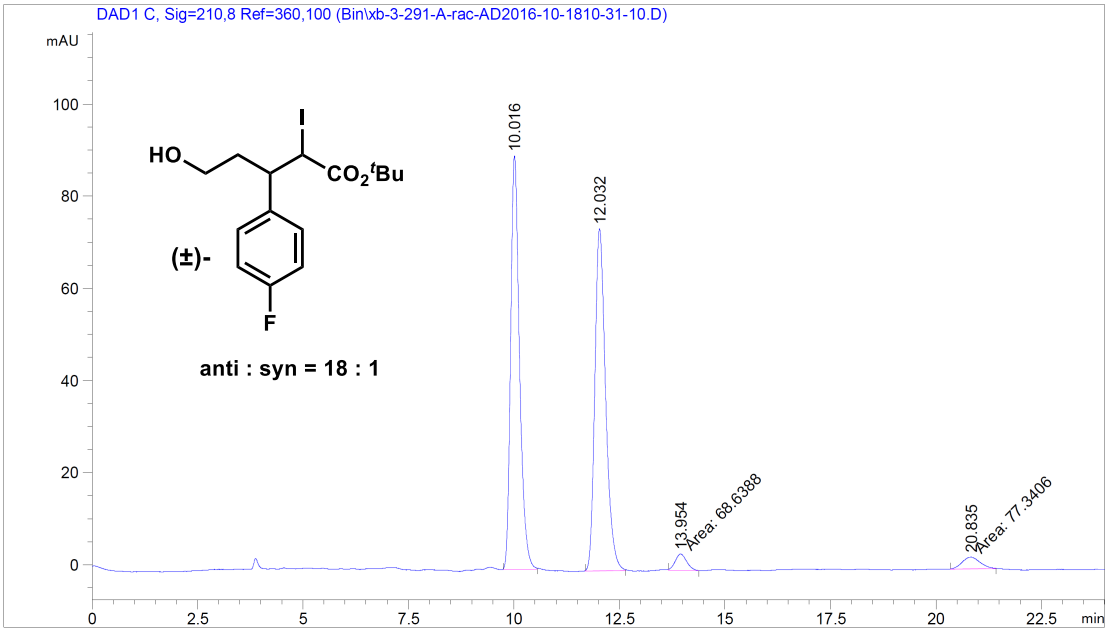


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	21.585	MM	0.7563	3025.88696	50.4182
2	23.466	MM	0.8946	2975.69312	49.5818

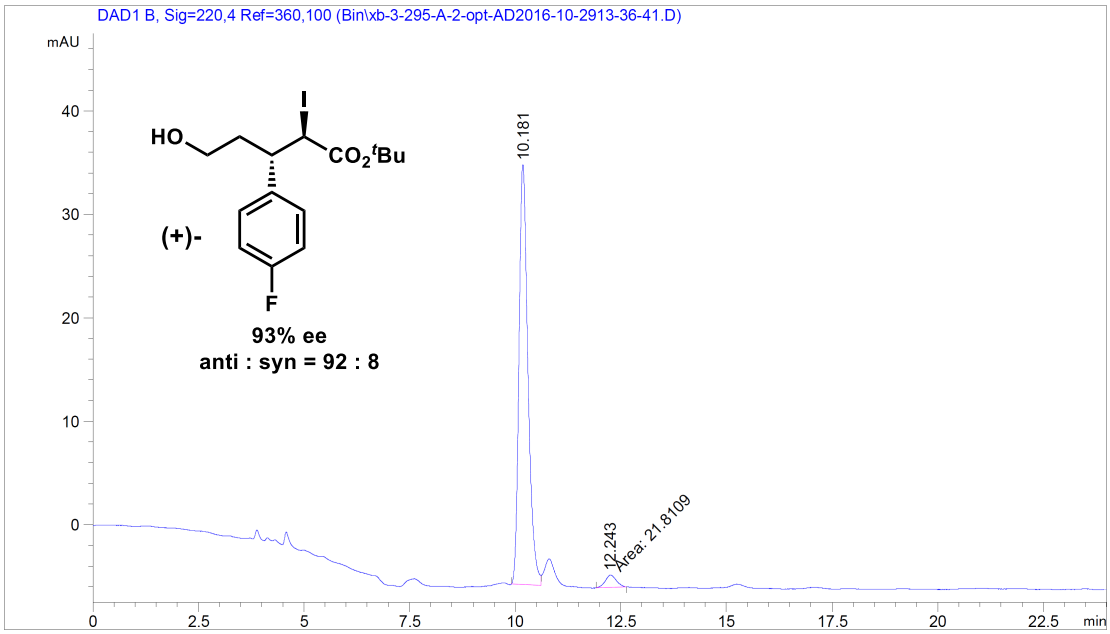


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	21.096	MM	0.7406	5388.05811	96.8237
2	22.951	MM	0.8223	176.75499	3.1763

(+)-*tert*-Butyl (2*R*, 3*S*)-3-(4-fluorophenyl)-5-hydroxy-2-iodopentanoate, 6h

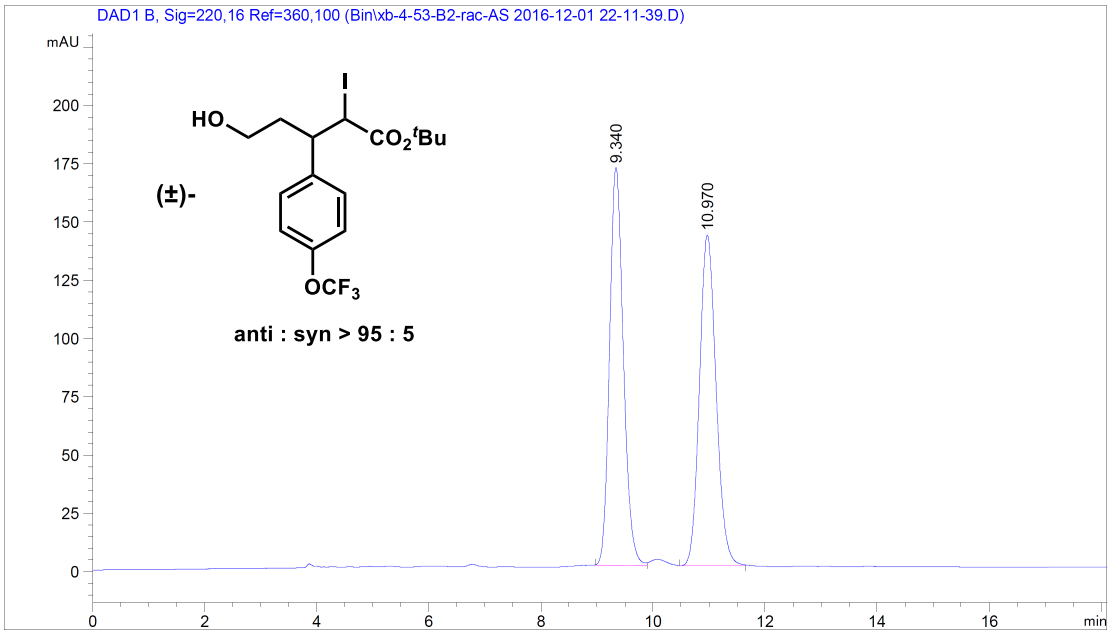


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	10.016	BB	0.2208	1306.37756	47.1625	?
2	12.032	BB	0.2698	1317.59180	47.5674	?
3	13.954	MM	0.3166	68.63876	2.4780	?
4	20.835	MM	0.4980	77.34064	2.7921	?

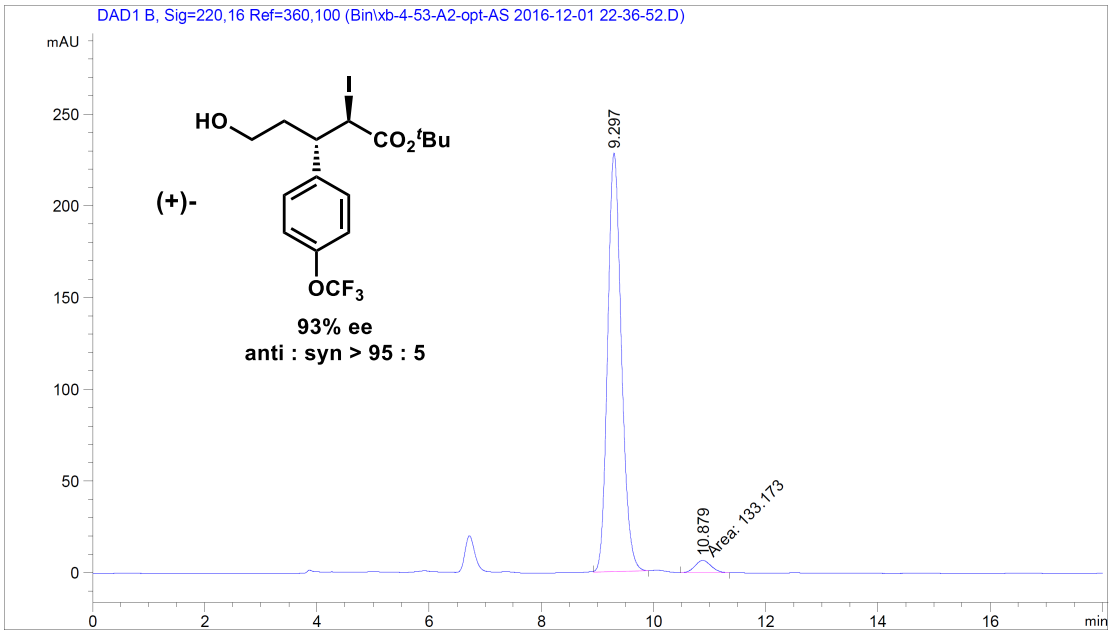


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	10.181	BB	0.2243	599.35931	96.4887	?
2	12.243	MM	0.3063	21.81087	3.5113	?

(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(4-(trifluoromethoxy)phenyl)pentanoate, 6i

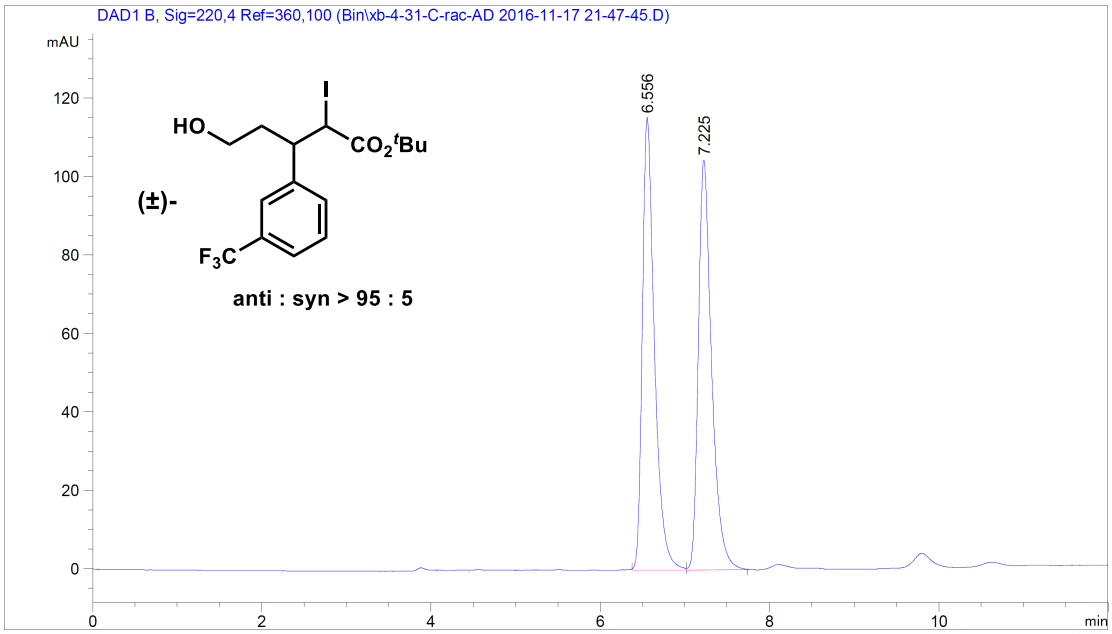


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.340	BB	0.2636	2922.66309	49.9983
2	10.970	VB	0.3194	2922.86060	50.0017

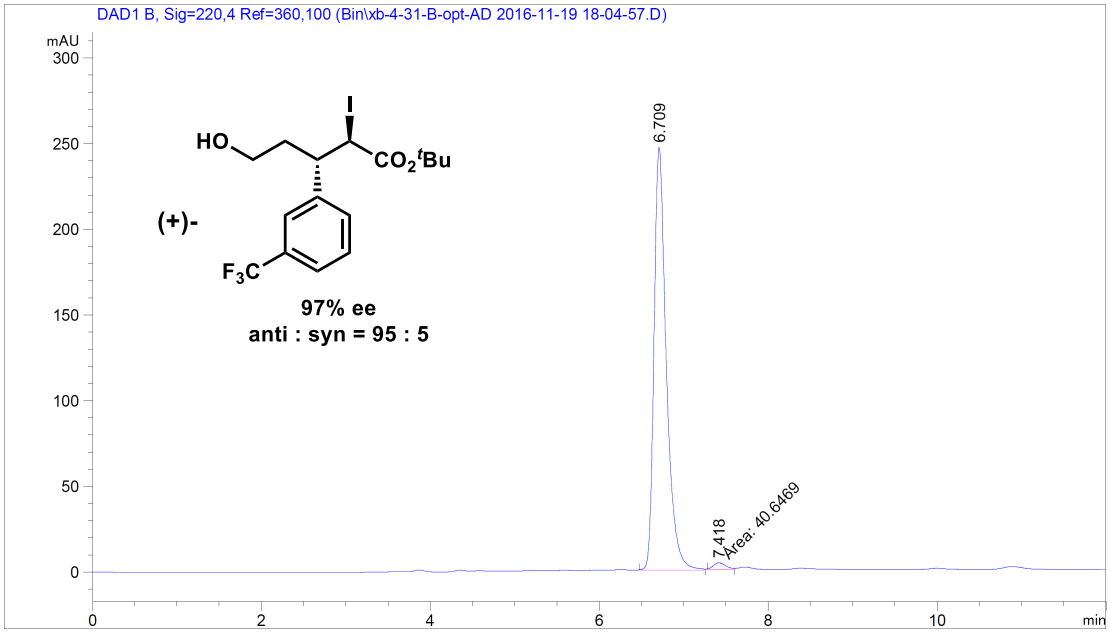


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.297	BB	0.2630	3890.41846	96.6902
2	10.879	MM	0.3313	133.17302	3.3098

(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(3-(trifluoromethyl)phenyl)pentanoate, 6j

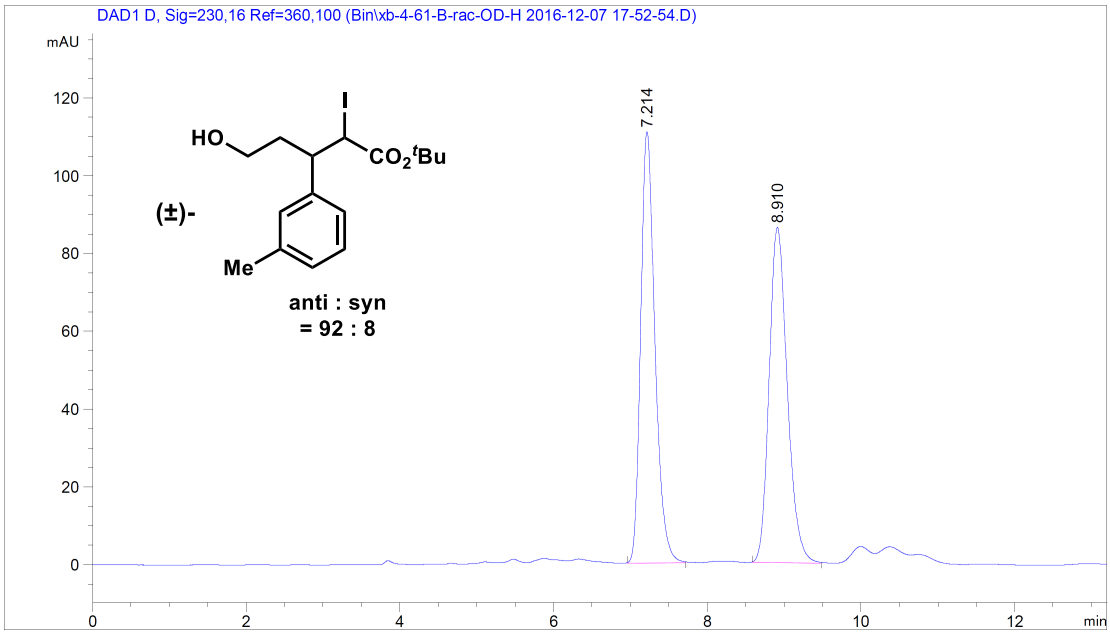


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.556	BV	0.1478	1145.57678	50.0529
2	7.225	VB	0.1645	1143.15527	49.9471

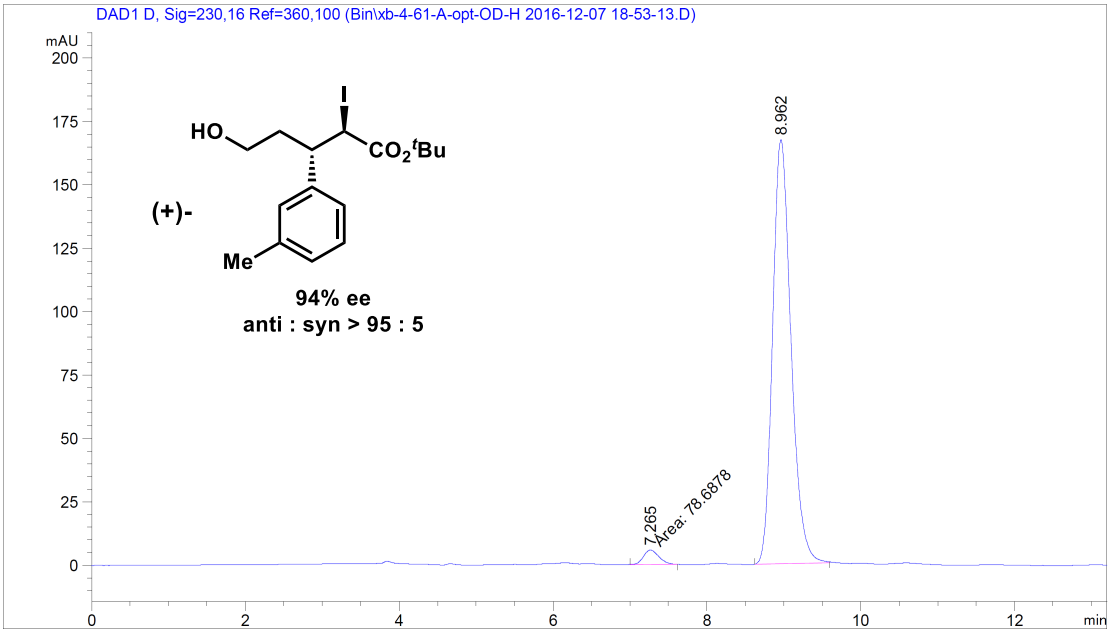


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.709	BB	0.1505	2486.08887	98.3913
2	7.418	MM	0.1711	40.64690	1.6087

(+)-*tert*-Butyl (2*R*, 3*S*)-5-hydroxy-2-iodo-3-(*m*-tolyl)pentanoate, 6k

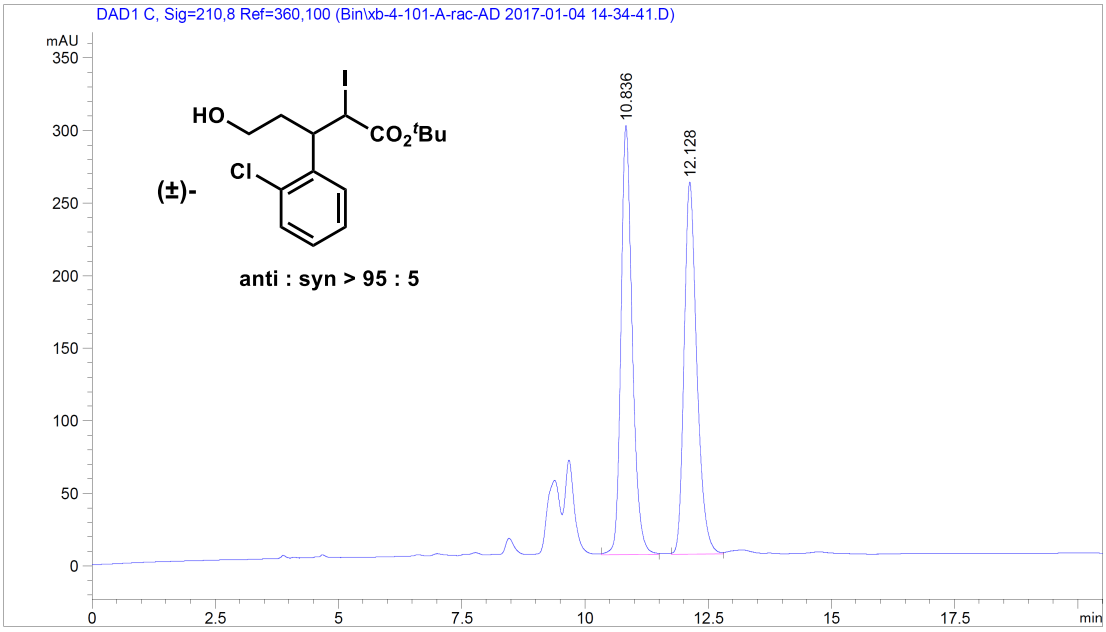


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.214	BB	0.1972	1426.82507	50.2572
2	8.910	BB	0.2521	1412.22205	49.7428

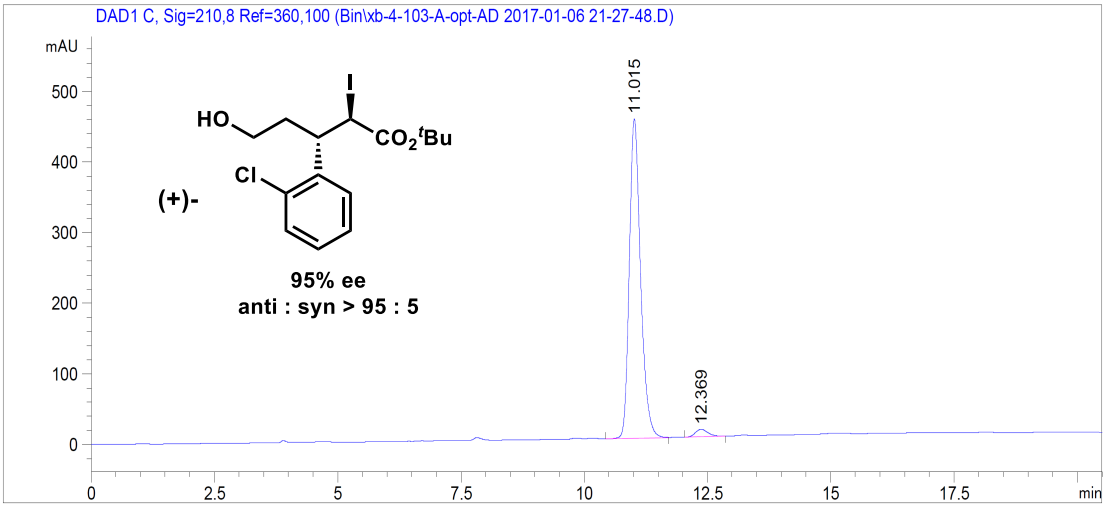


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.265	MM	0.2299	78.68779	2.7558
2	8.962	BB	0.2546	2776.62085	97.2442

(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-chlorophenyl)-5-hydroxy-2-iodopentanoate, 6l

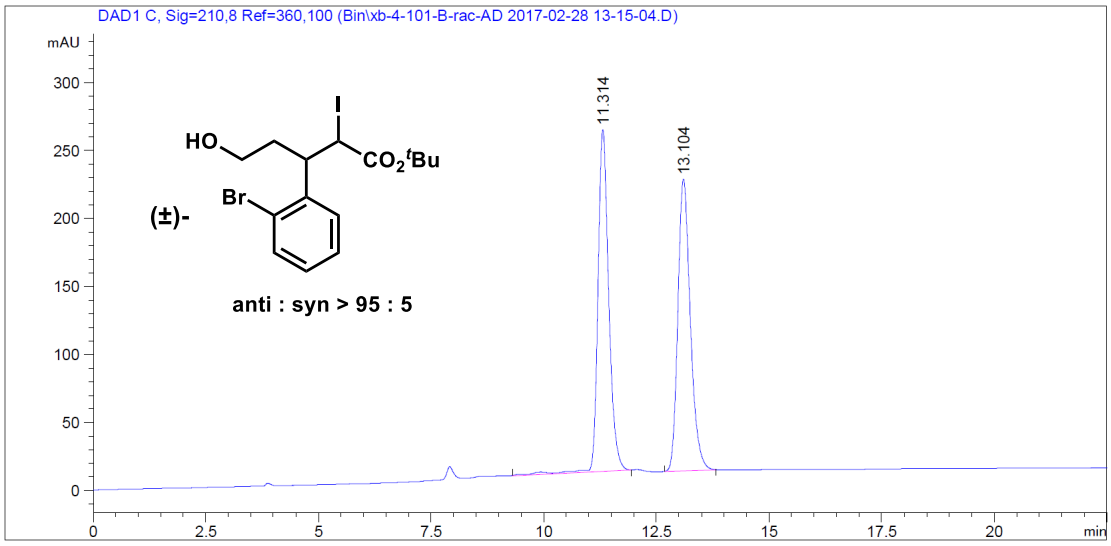


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	10.836	BB	0.2416	4704.47412	50.4599
2	12.128	BB	0.2743	4618.71045	49.5401

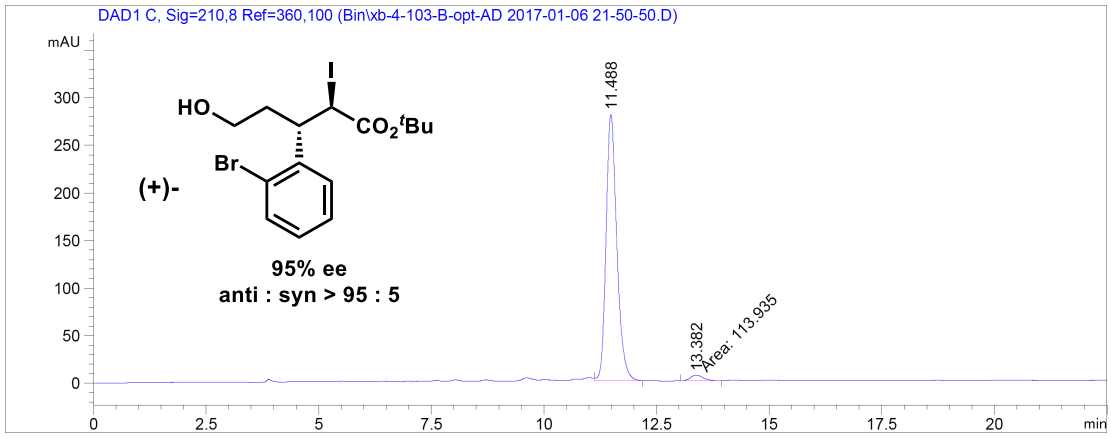


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	11.015	VB	0.2437	7203.25586	97.4041
2	12.369	BB	0.2735	191.97359	2.5959

(+)-*tert*-Butyl (2*R*, 3*S*)-3-(2-bromophenyl)-5-hydroxy-2-iodopentanoate, 6m

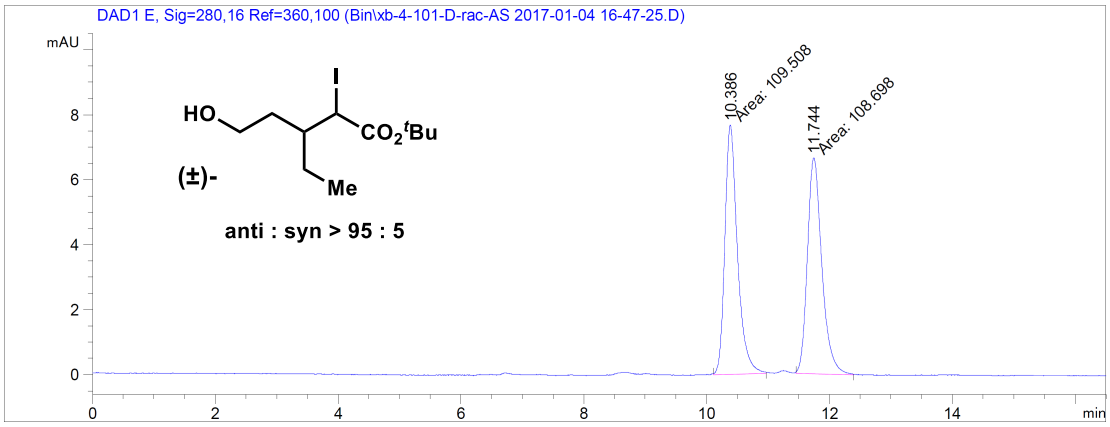


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	11.314	BB	0.2536	4192.00830	50.3711	?
2	13.104	BB	0.2944	4130.23828	49.6289	?

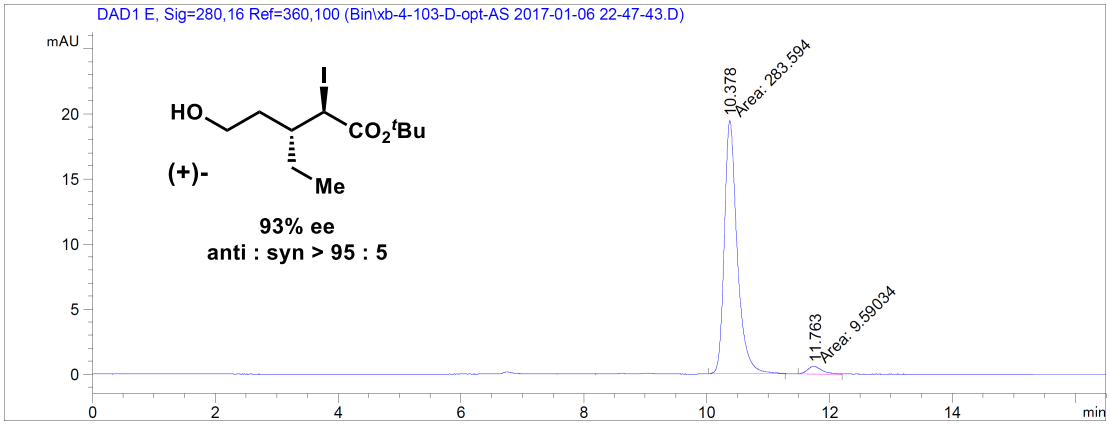


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	11.488	VB	0.2530	4651.80518	97.6093
2	13.382	MM	0.3184	113.93534	2.3907

(+)-*tert*-Butyl (2*R*, 3*R*)-3-ethyl-5-hydroxy-2-iodopentanoate, 6n

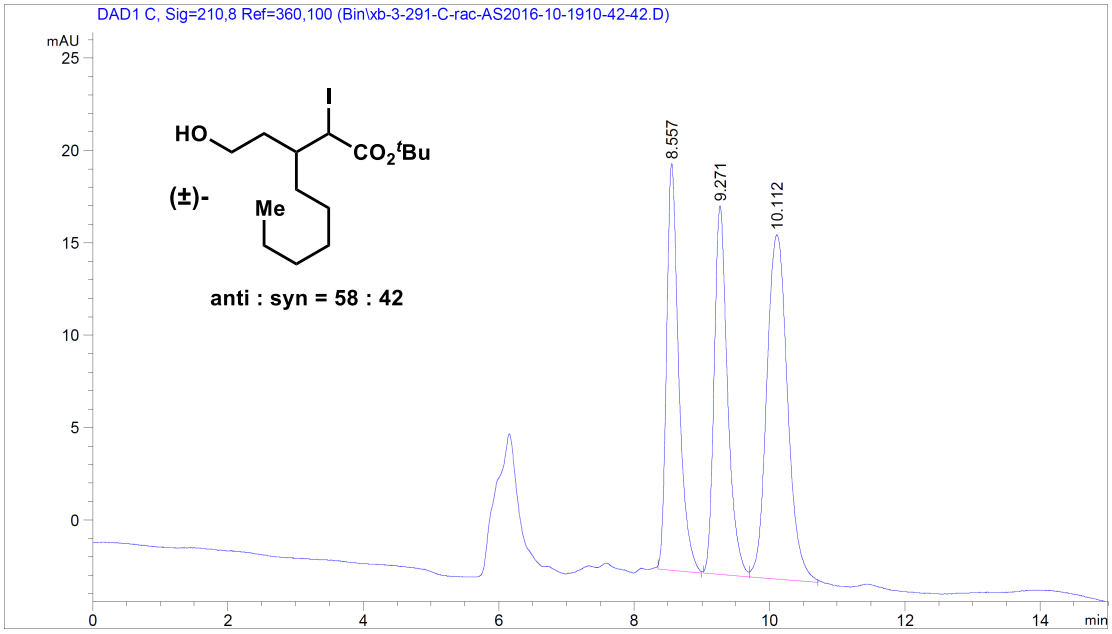


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	10.386	MM	0.2379	109.50795	50.1857
2	11.744	MM	0.2723	108.69774	49.8143

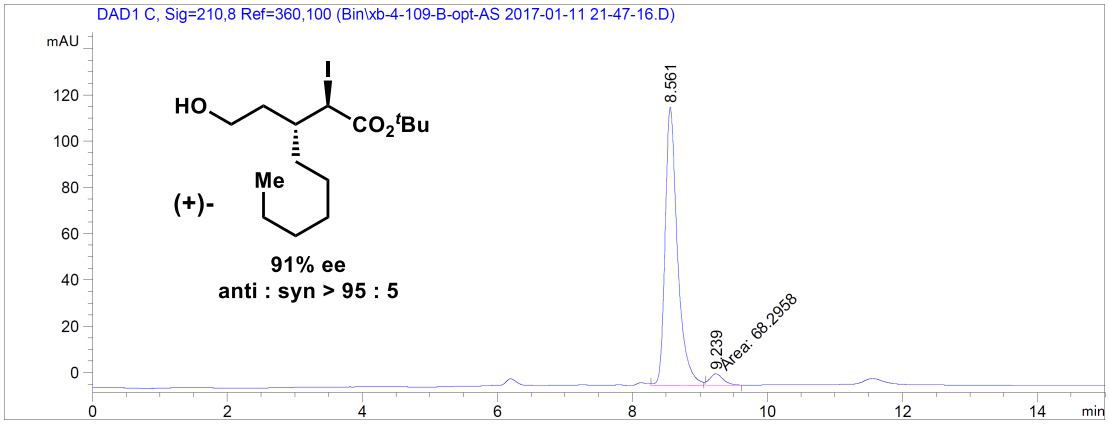


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	10.378	MM	0.2430	283.59424	96.7289
2	11.763	MM	0.2735	9.59034	3.2711

(+)-*tert*-Butyl (2*R*, 3*R*)-3-(2-hydroxyethyl)-2-iodononanoate, 6o

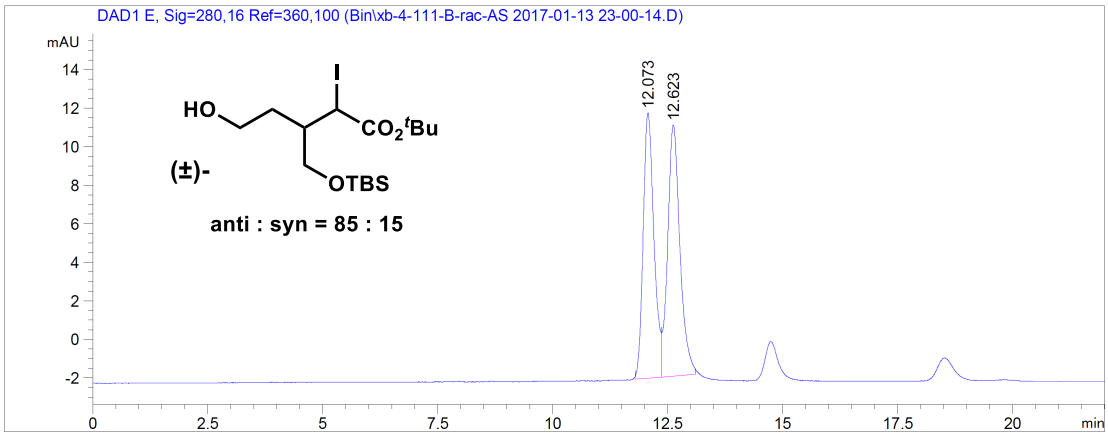


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.557	BB	0.1858	275.26901	29.0346
2	9.271	BB	0.2090	275.31021	29.0390
3	10.112	BB	0.3389	397.49271	41.9264

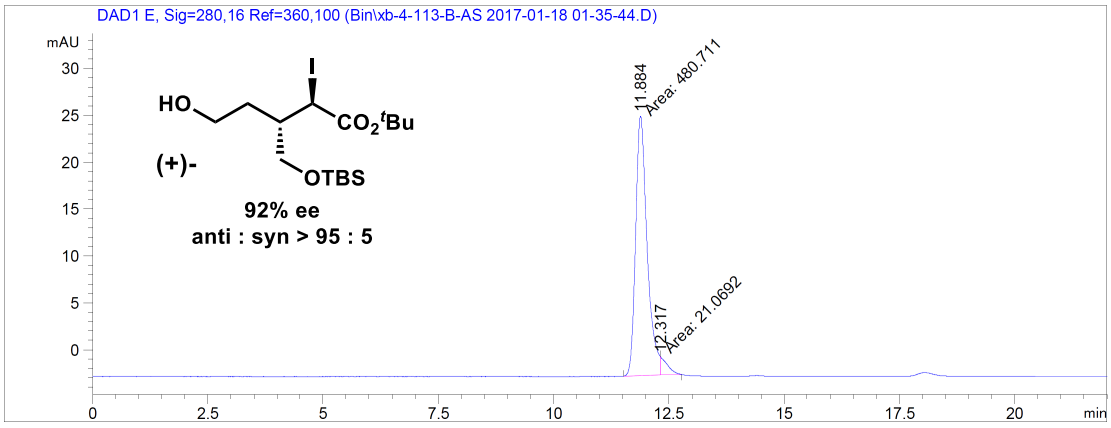


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.561	VV	0.1896	1532.30237	95.7331
2	9.239	MM	0.2277	68.29581	4.2669

(+)-*tert*-Butyl (2*R*, 3*S*)-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-hydroxy-2-iodopentanoate, 6p

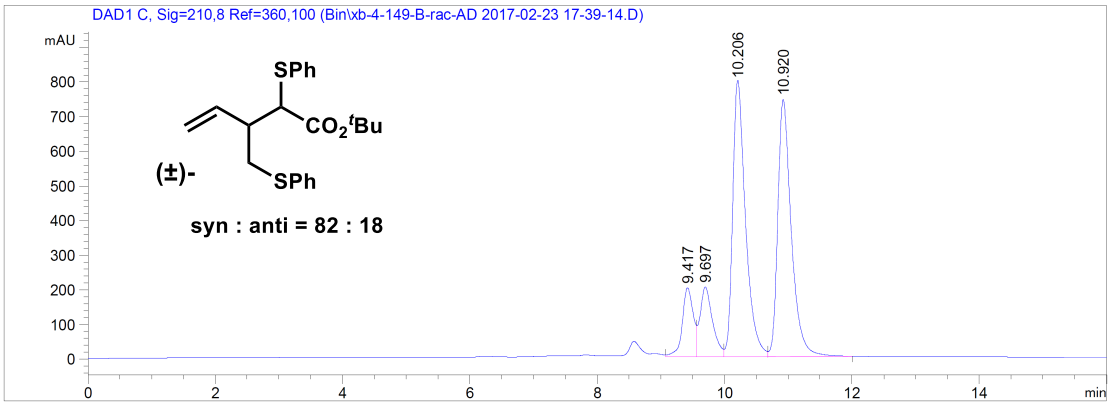


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	12.073	BV	0.2443	223.45082	48.0523	?
2	12.623	VB	0.2762	241.56548	51.9477	?

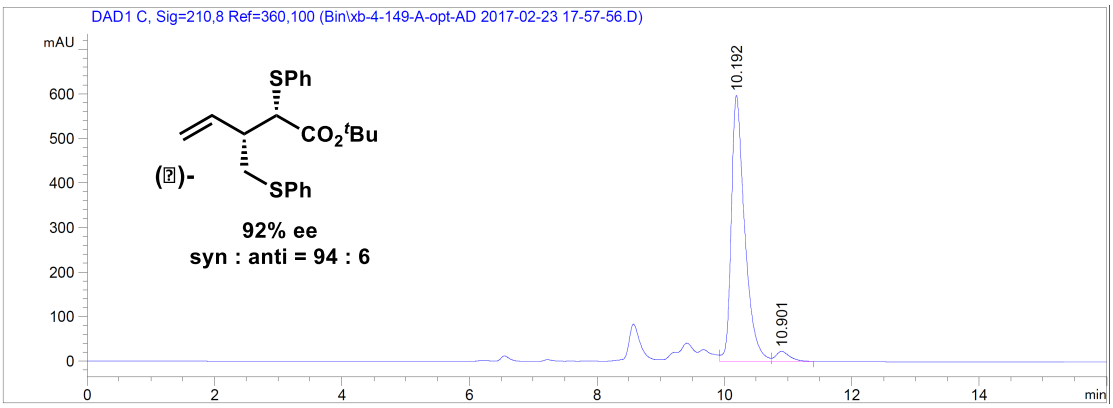


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	11.884	MM	0.2895	480.71057	95.8011	?
2	12.317	MM	0.1282	21.06917	4.1989	?

(–)-*tert*-Butyl (2*S*, 3*S*)-2-(phenylthio)-3-((phenylthio)methyl)pent-4-enoate, 7q

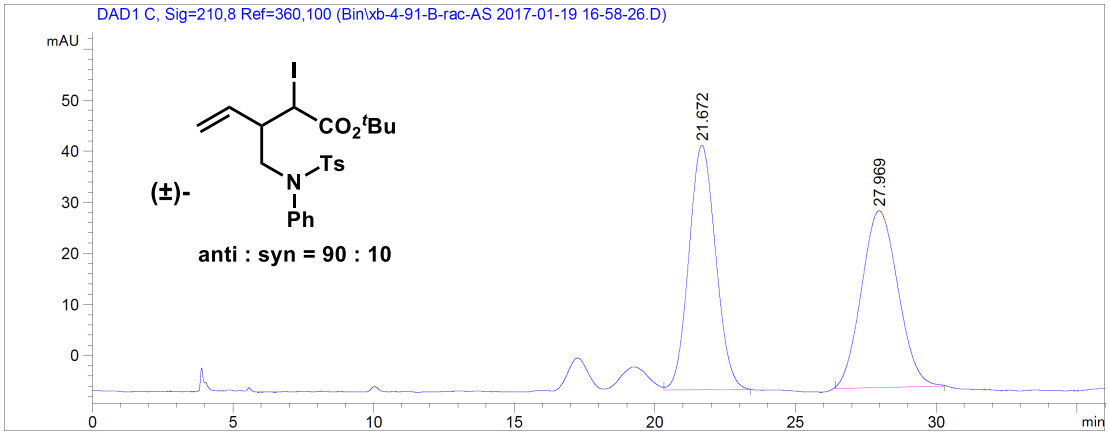


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	9.417	VV	0.1818	2427.18872	8.8783	?
2	9.697	VV	0.1990	2748.83838	10.0548	?
3	10.206	VV	0.2085	1.11829e4	40.9053	?
4	10.920	VB	0.2206	1.09796e4	40.1616	?

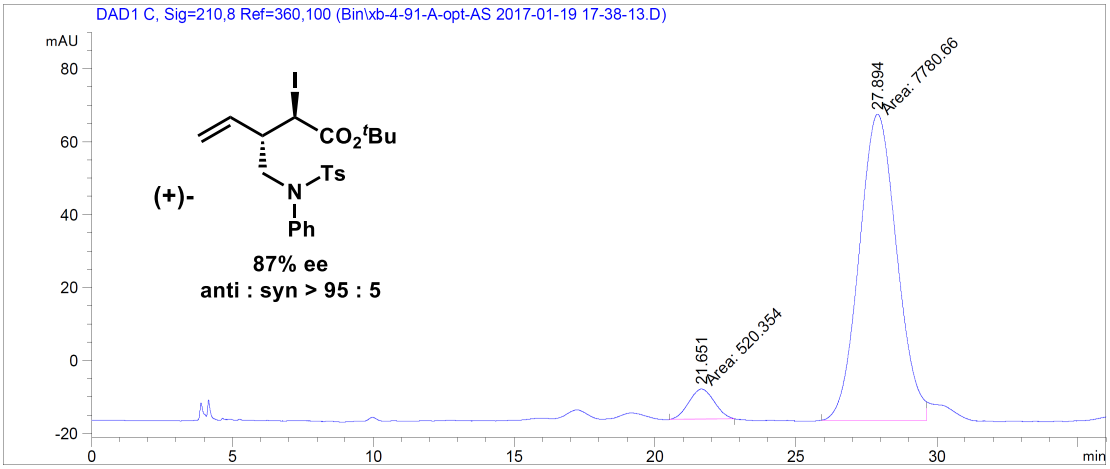


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	10.192	VV	0.2141	8771.83398	96.0474	?
2	10.901	VB	0.2269	360.98492	3.9526	?

(+)-*tert*-Butyl (2*R*, 3*S*)-2-iodo-3-(((4-methyl-*N*-phenylphenyl)sulfonamido)methyl)pent-4-enoate, 5r

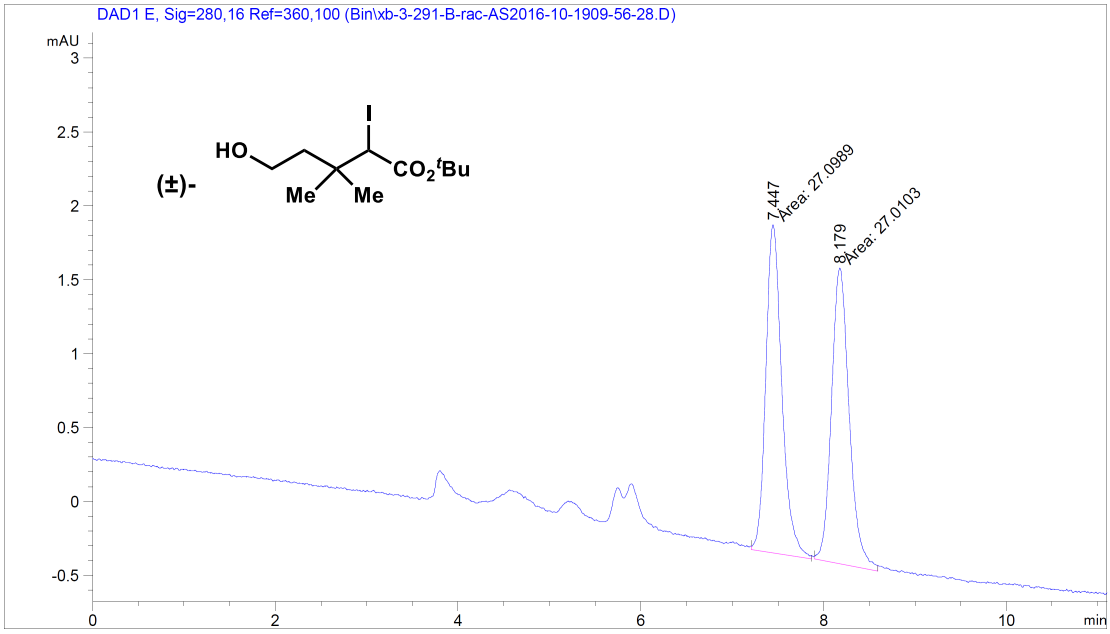


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	21.672	VB	0.9756	3178.42651	50.3356	?
2	27.969	BB	1.0776	3136.04785	49.6644	?

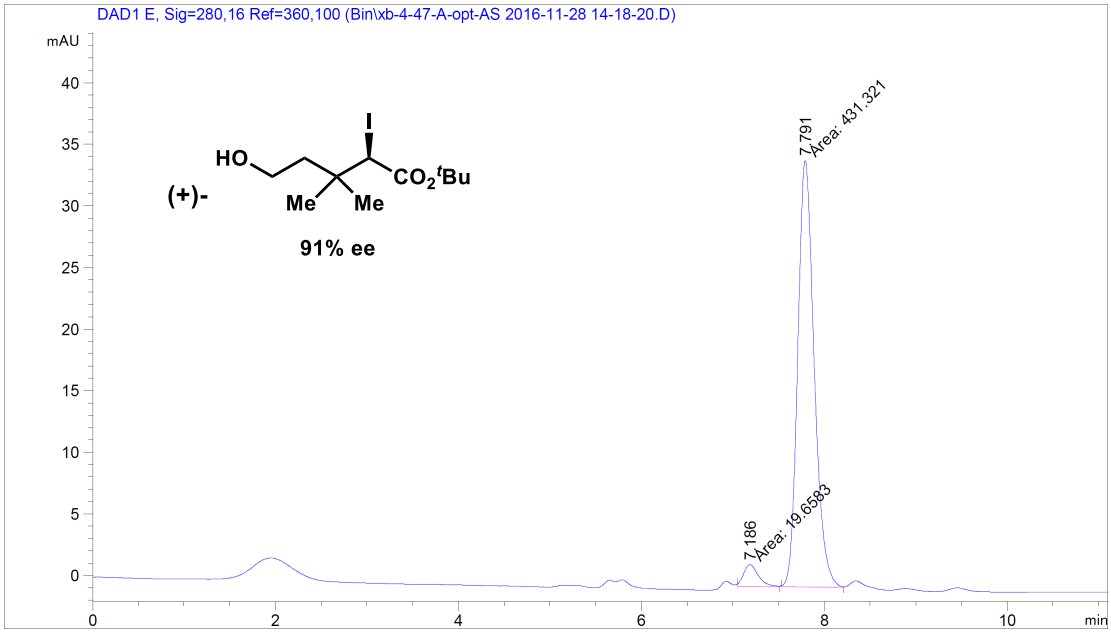


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	21.651	MM	1.0455	520.35382	6.2686	?
2	27.894	MM	1.5447	7780.65918	93.7314	?

(+)-*tert*-Butyl (*R*)-5-hydroxy-2-iodo-3,3-dimethylpentanoate, 6s

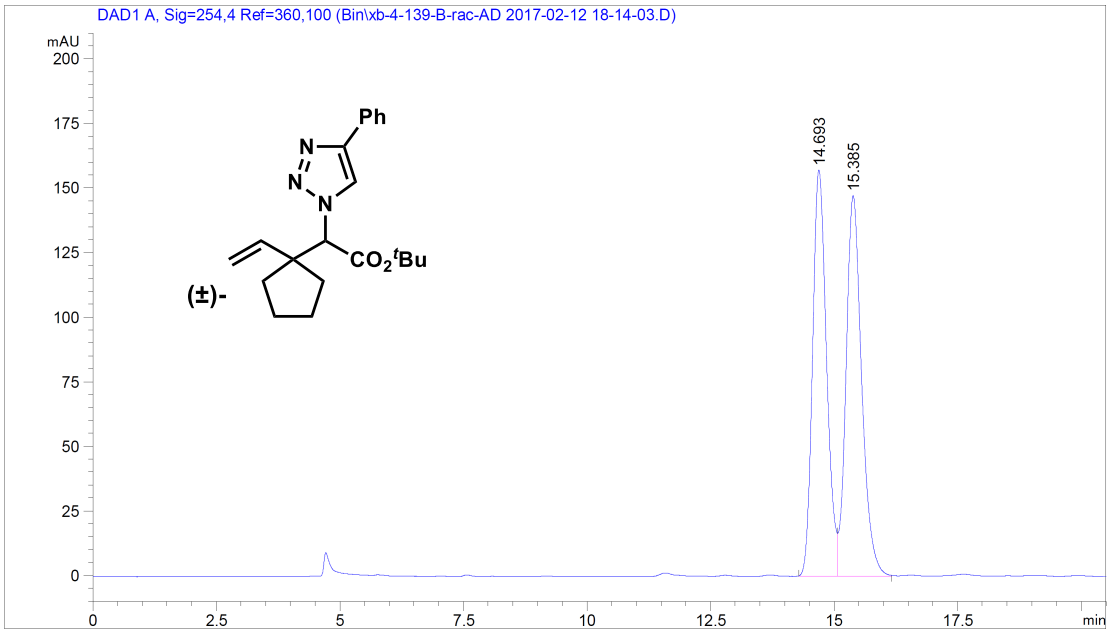


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.447	MM	0.2036	27.09895	50.0819
2	8.179	MM	0.2249	27.01027	49.9181

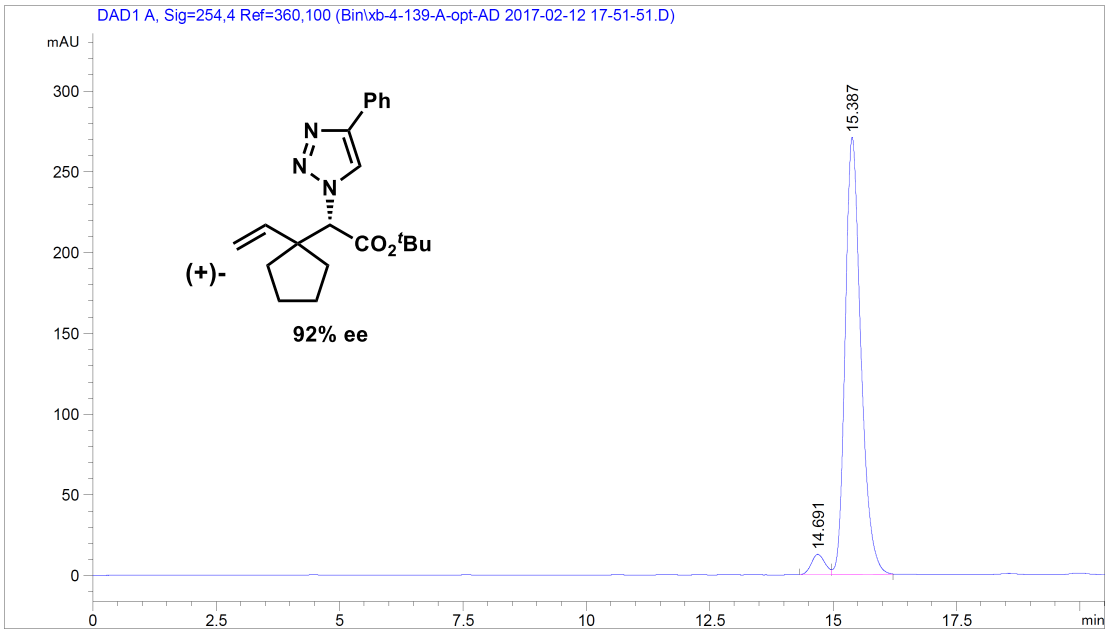


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.186	MM	0.1865	19.65832	4.3590
2	7.791	MM	0.2077	431.32062	95.6410

(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcyclopentyl)acetate, S11t

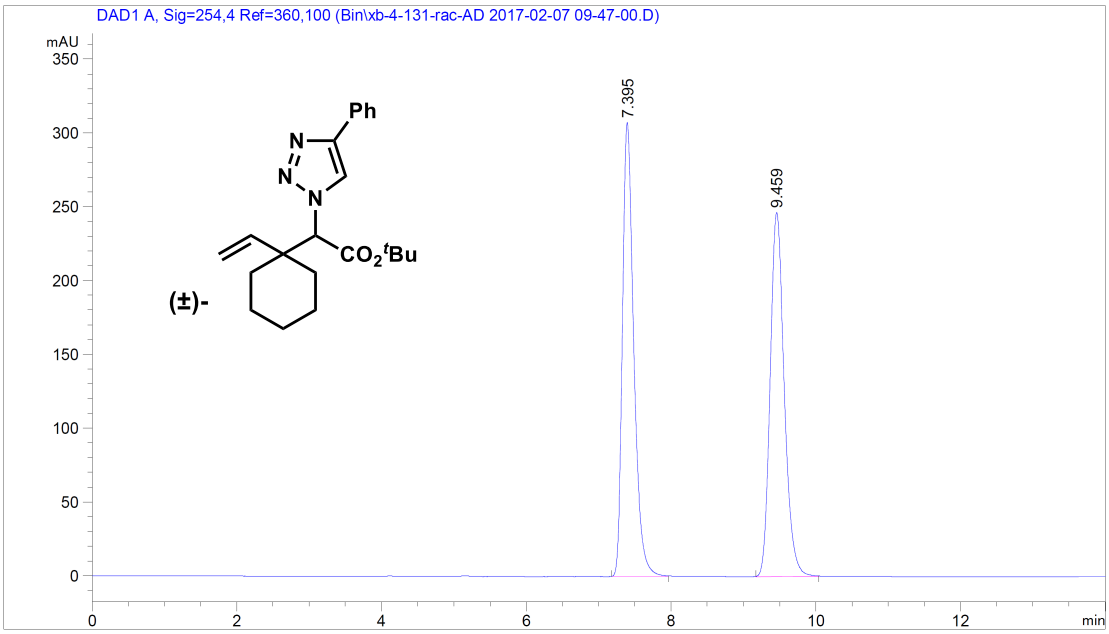


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.693	BV	0.3010	3099.58105	48.9918	?
2	15.385	VB	0.3317	3227.15137	51.0082	?

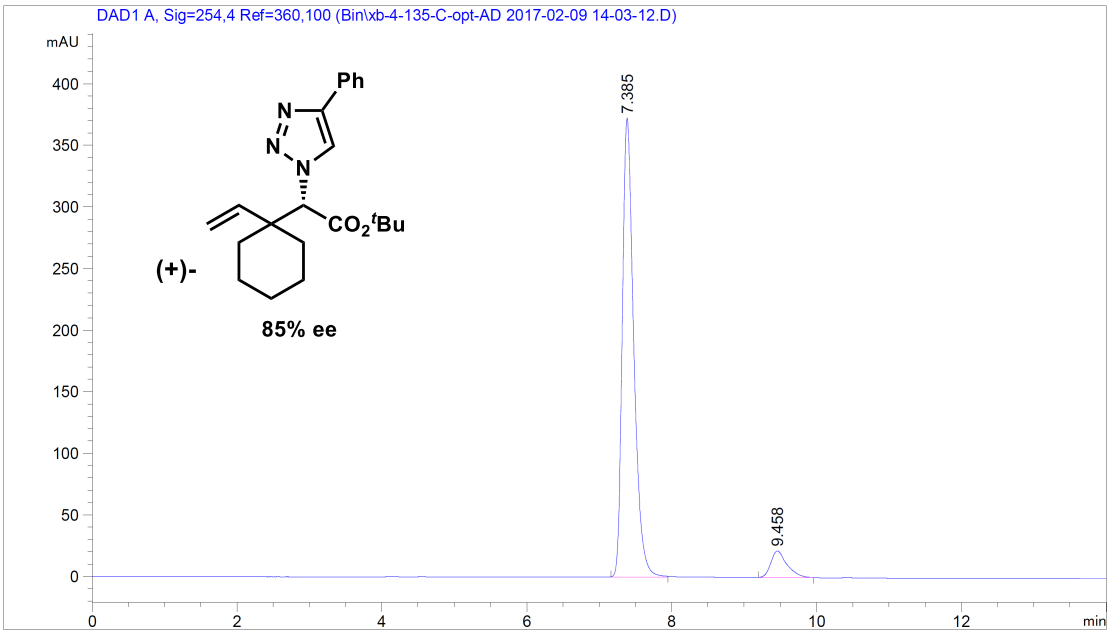


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.691	BV	0.2970	241.88809	3.8866	?
2	15.387	VB	0.3366	5981.82373	96.1134	?

(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcyclohexyl)acetate, S11u

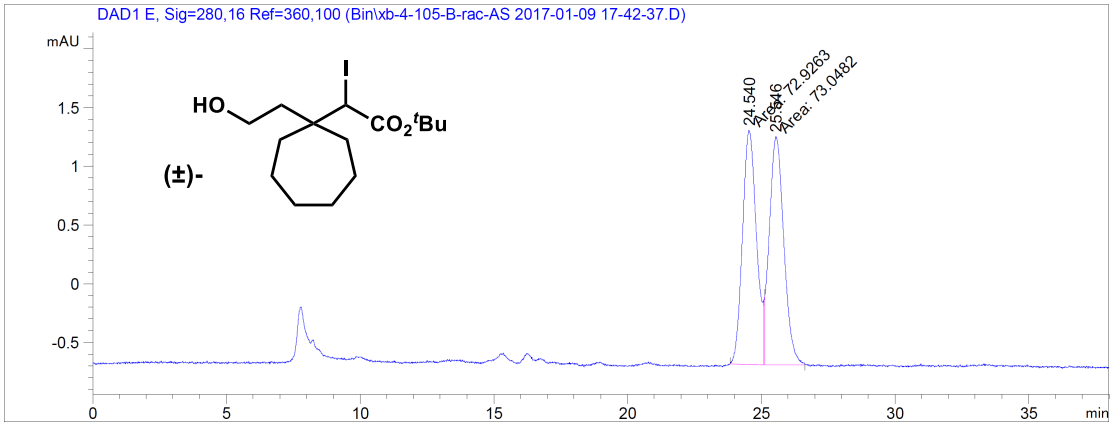


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	7.395	BB	0.1643	3328.78564	50.0314	?
2	9.459	BB	0.2073	3324.60376	49.9686	?

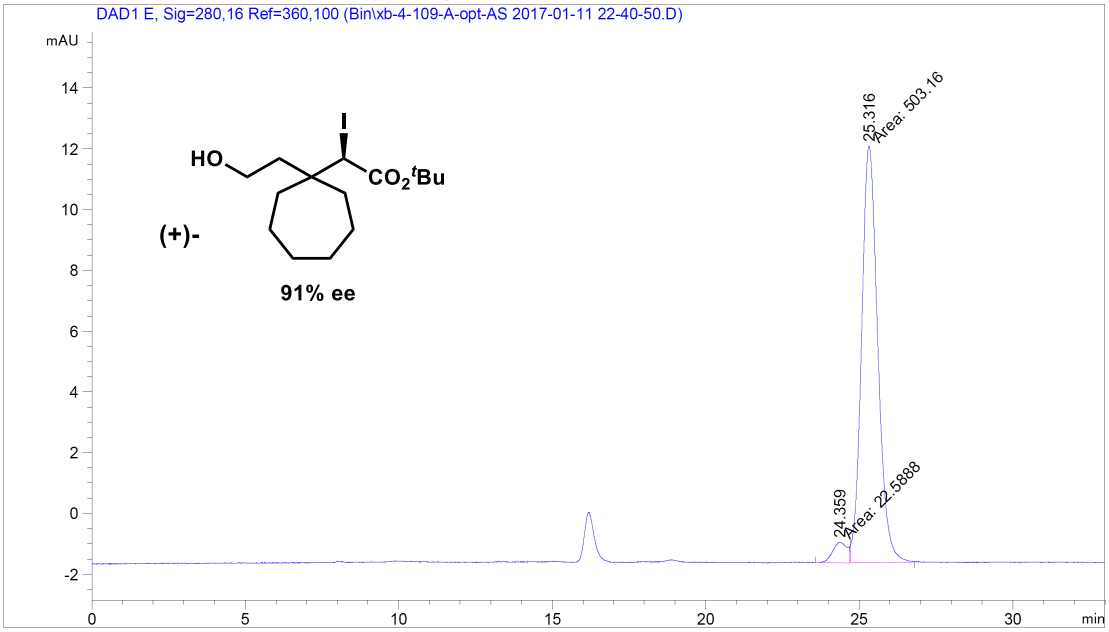


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	7.385	BB	0.1651	4056.86499	92.3823	?
2	9.458	BB	0.2289	334.52350	7.6177	?

(+)-*tert*-Butyl (*R*)-2-(1-(2-hydroxyethyl)cycloheptyl)-2-iodoacetate, 6v

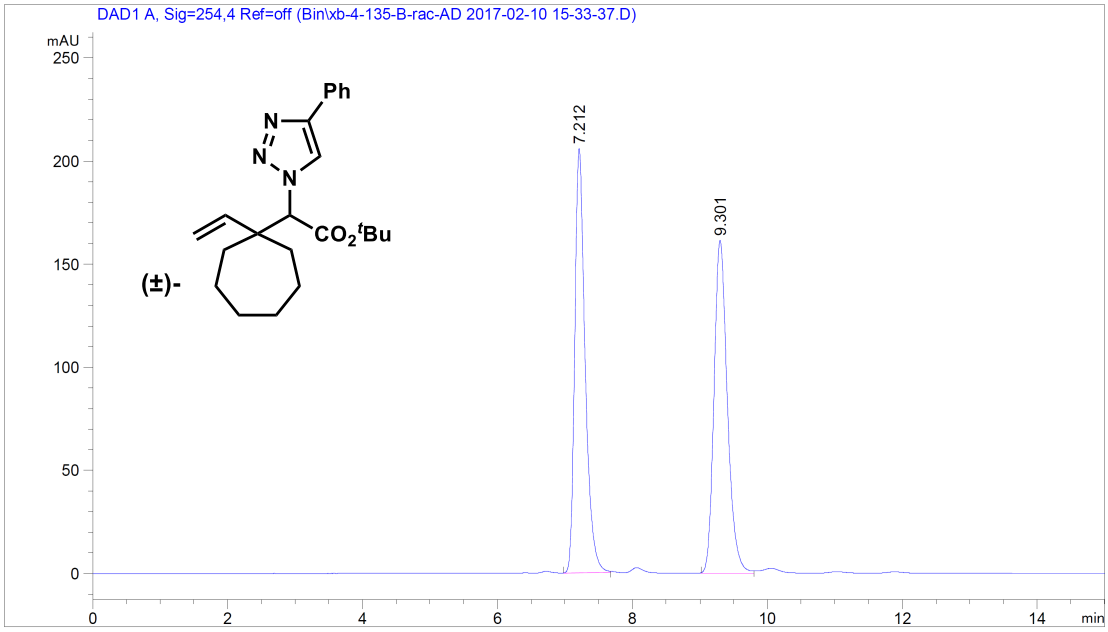


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	24.540	MM	0.6094	72.92627	49.9583
2	25.546	MM	0.6269	73.04816	50.0417

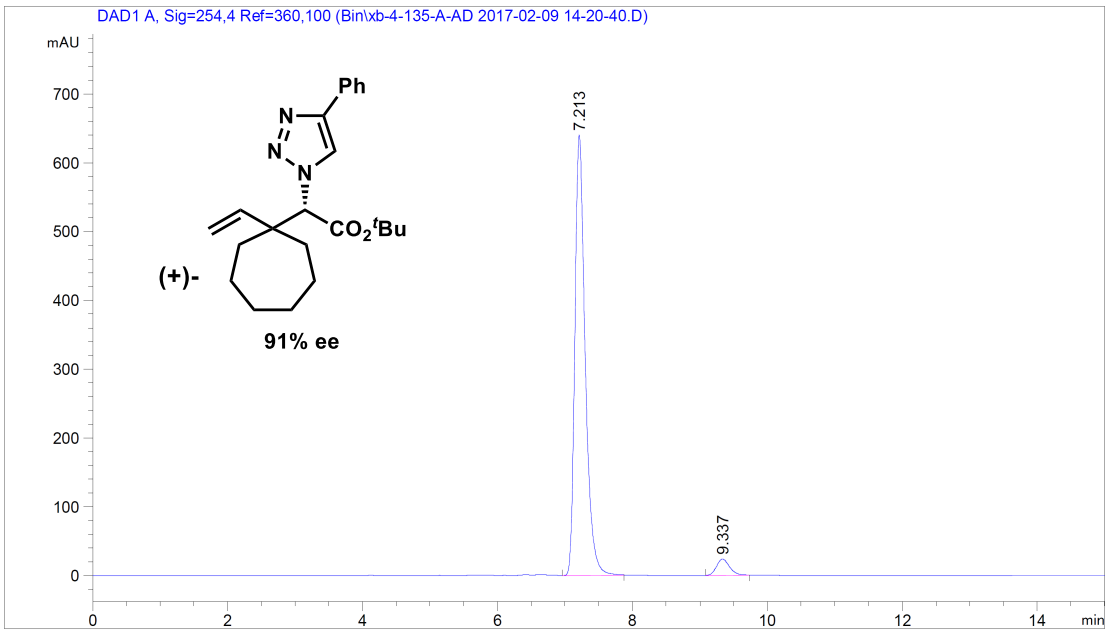


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	24.359	MM	0.5500	22.58876	4.2965	?
2	25.316	MM	0.6118	503.15973	95.7035	?

(+)-*tert*-Butyl (*S*)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-(1-vinylcycloheptyl)acetate, S11v

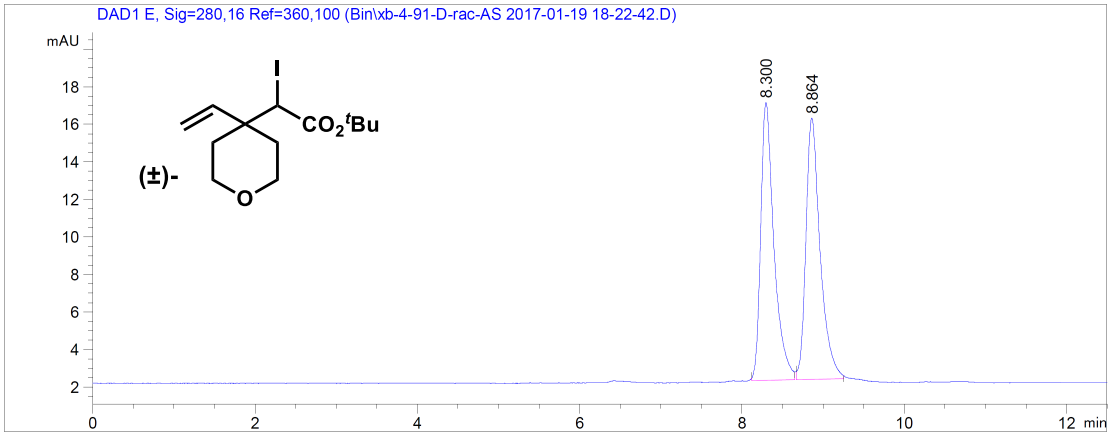


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	7.212	BB	0.1612	2207.51318	49.8645	?
2	9.301	BB	0.2104	2219.51123	50.1355	?

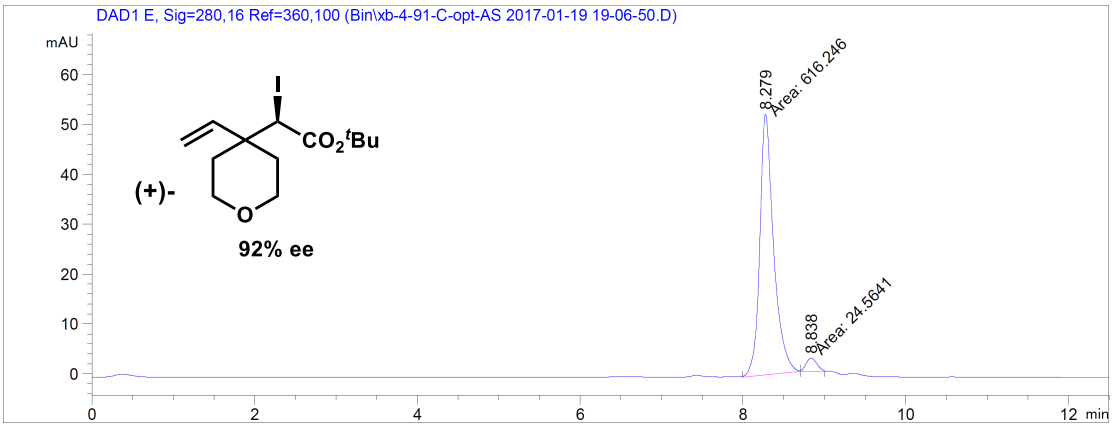


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	7.213	VB	0.1612	6809.32959	95.5050	?
2	9.337	BB	0.2076	320.48422	4.4950	?

(+)-*tert*-Butyl (*R*)-2-iodo-2-(4-vinyltetrahydro-2H-pyran-4-yl)acetate, 5w

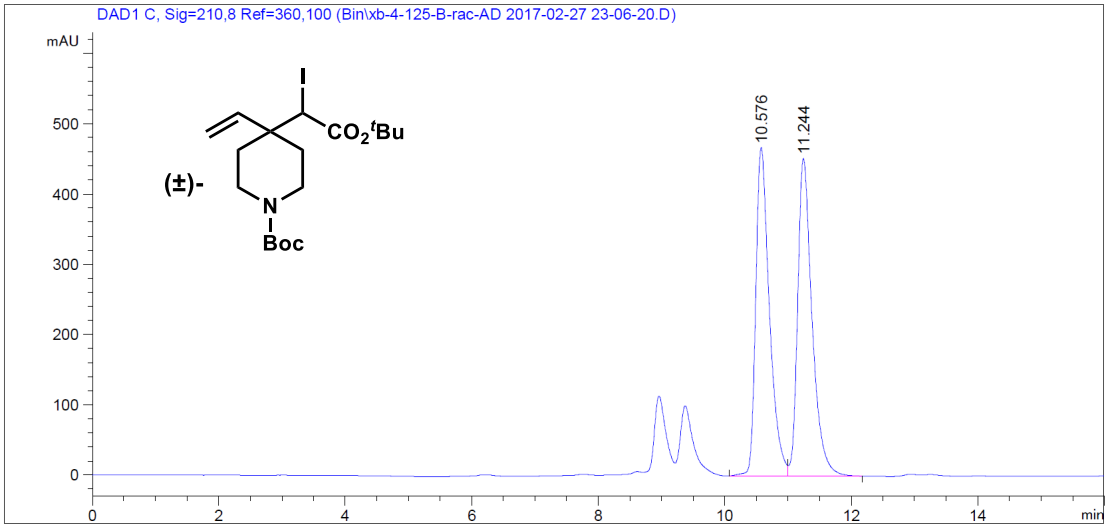


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	8.300	BB	0.1669	167.51727	49.6578	?
2	8.864	BB	0.1802	169.82574	50.3422	?

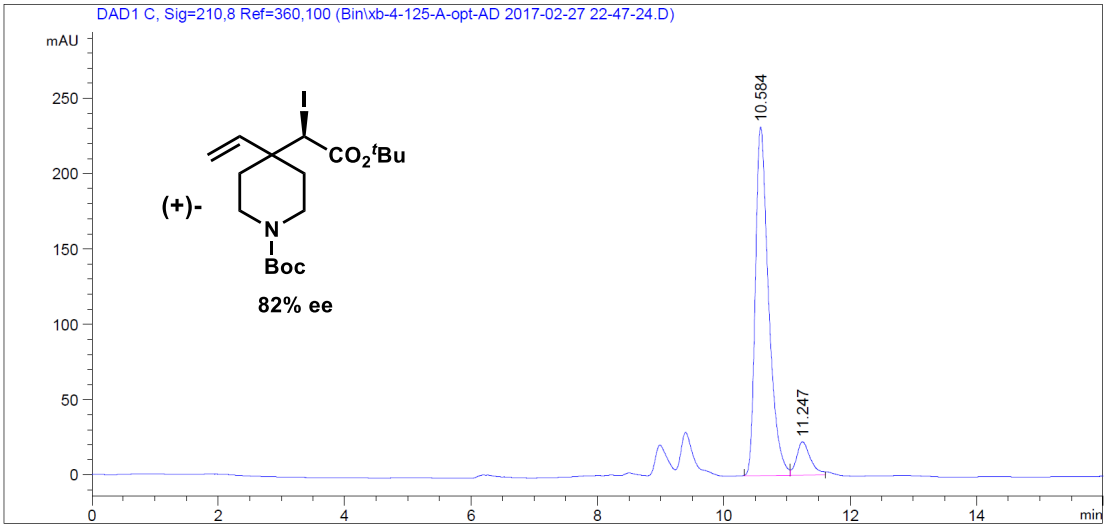


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	8.279	MM	0.1964	616.24634	96.1667	?
2	8.838	MM	0.1529	24.56411	3.8333	?

(+)-*tert*-Butyl
(*R*)-4-(2-(*tert*-butoxy)-1-iodo-2-oxoethyl)-4-vinylpiperidine-1-carboxylate, 5x

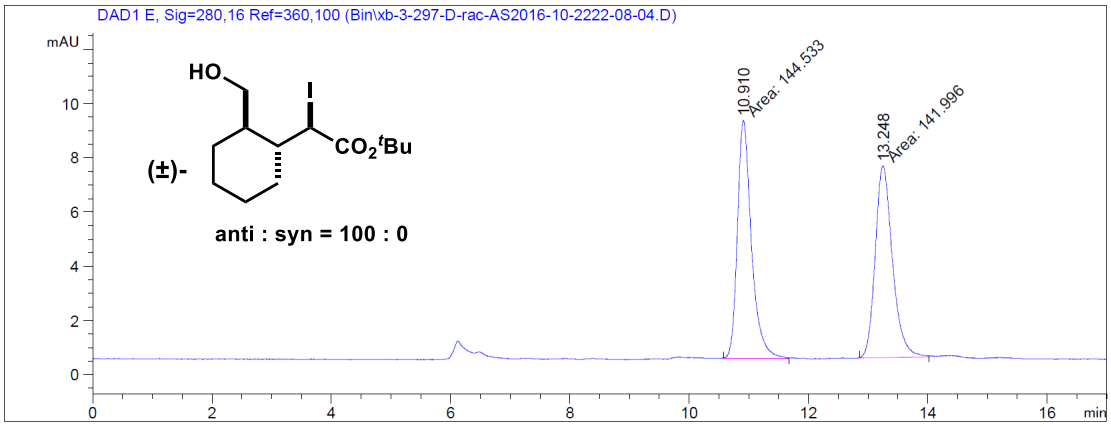


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	10.576	BV	0.2238	7045.74268	49.5911	?
2	11.244	VB	0.2358	7161.93359	50.4089	?

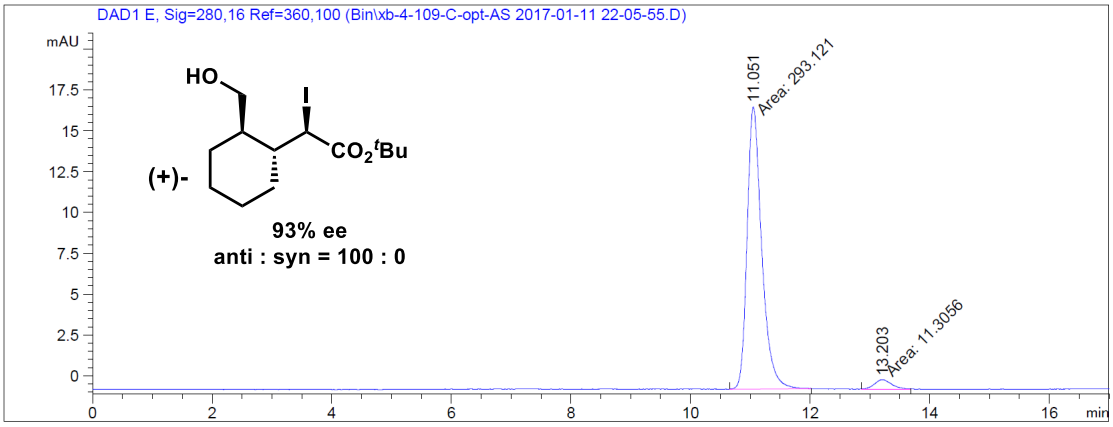


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	10.584	BV	0.2189	3372.50293	90.9607	?
2	11.247	VB	0.2269	335.14502	9.0393	?

(+)-*tert*-Butyl (2*R*)-2-((1*R*)-2-(hydroxymethyl)cyclohexyl)-2-iodoacetate, 6y

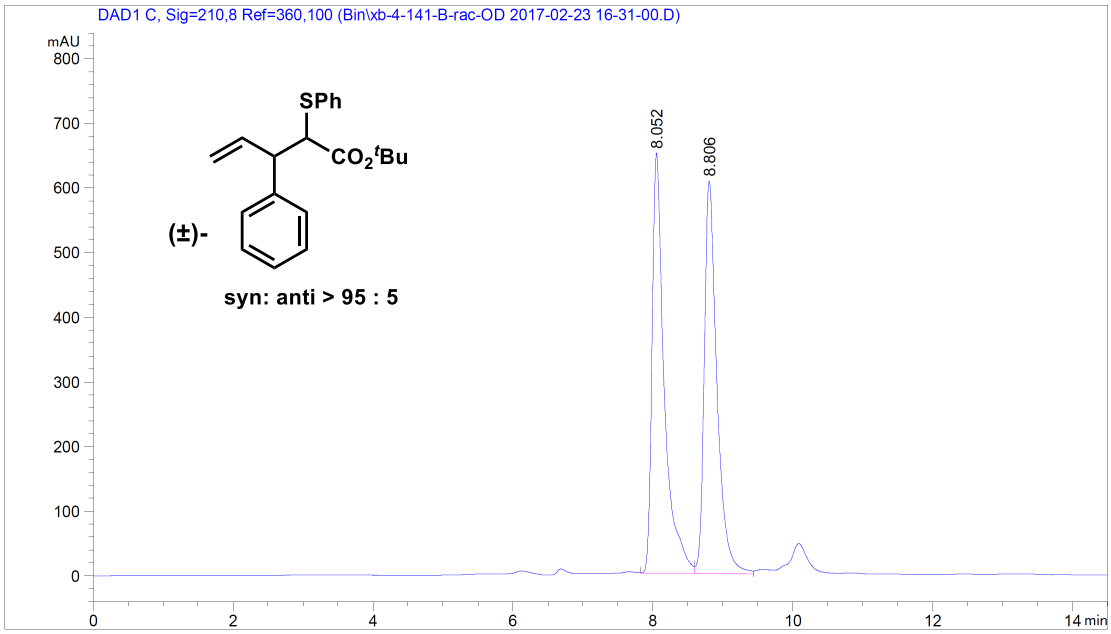


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	10.910	MM	0.2738	144.53304	50.4428
2	13.248	MM	0.3346	141.99571	49.5572

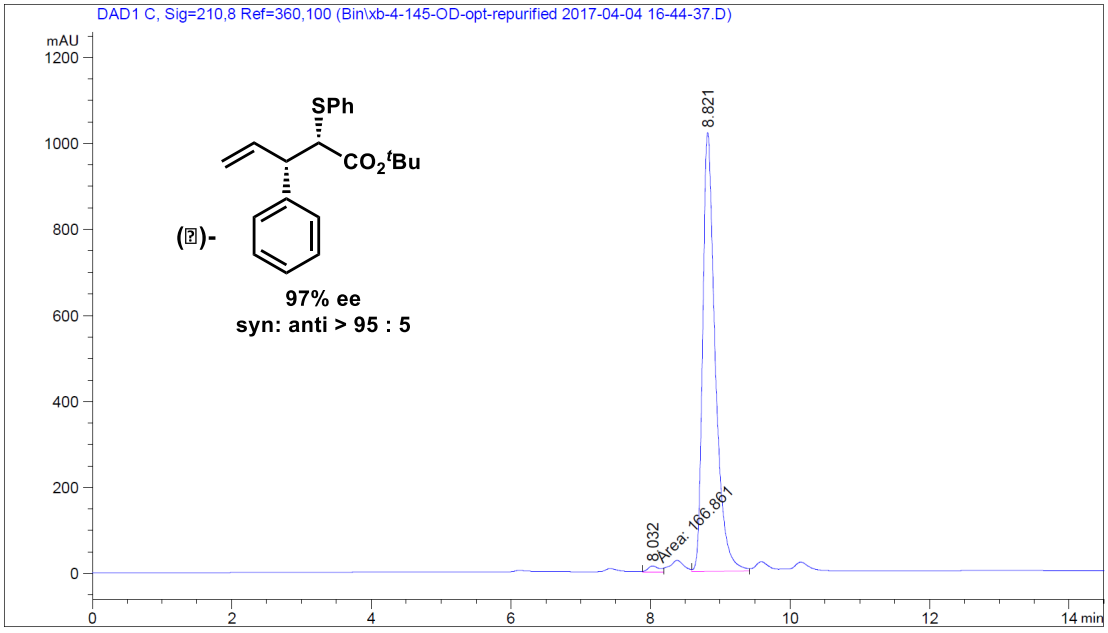


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	11.051	MM	0.2830	293.12079	96.2863
2	13.203	MM	0.3300	11.30558	3.7137

(–)-*tert*-Butyl (2*S*, 3*S*)-3-phenyl-2-(phenylthio)pent-4-enoate, 7a

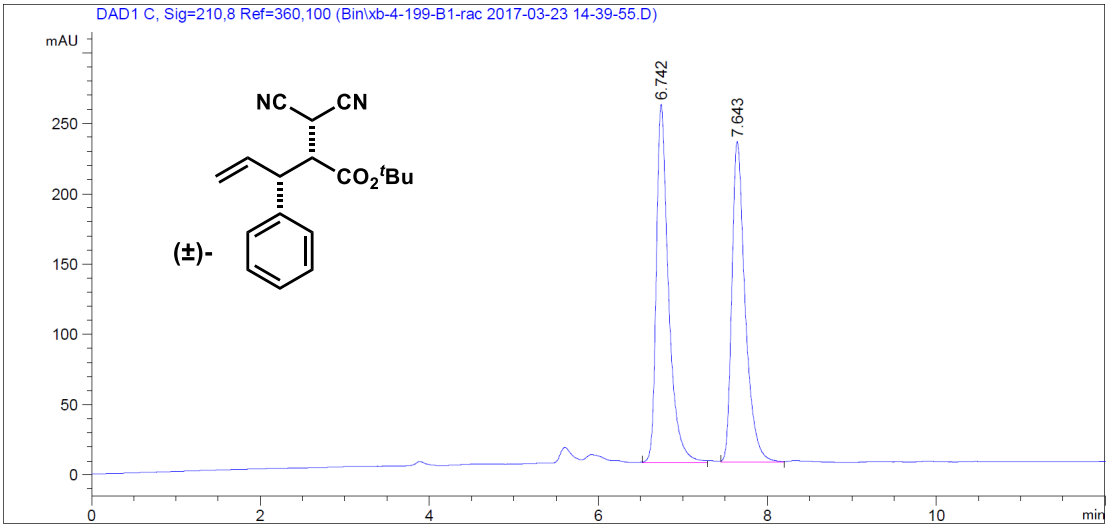


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	8.052	VV	0.1774	7945.91992	50.9543	?
2	8.806	VV	0.1869	7648.28760	49.0457	?

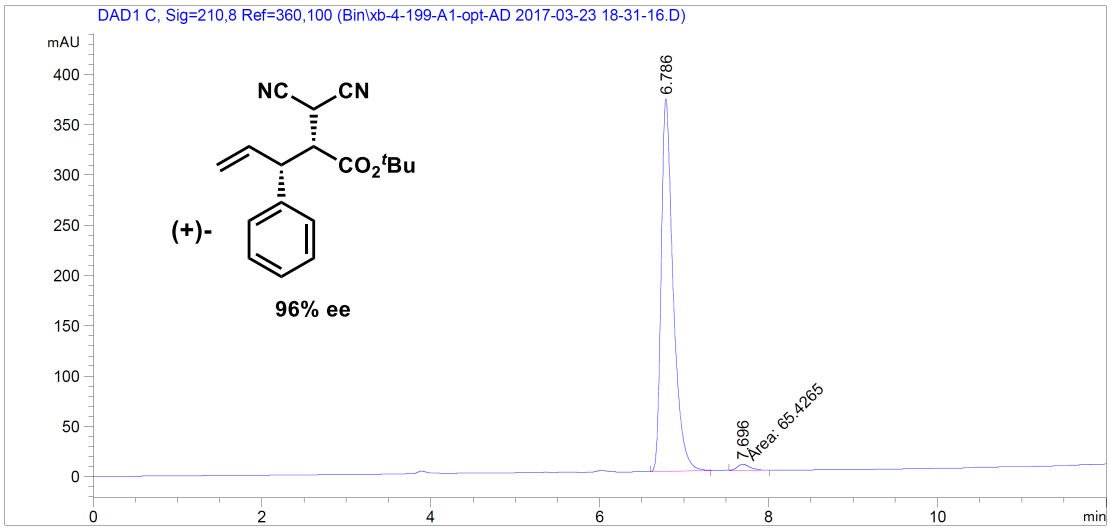


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	8.032	MM	0.1915	166.86095	1.2900	?
2	8.821	VV	0.1868	1.27678e4	98.7100	?

(+)-*tert*-Butyl (2*R*, 3*R*)-2-(dicyanomethyl)-3-phenylpent-4-enoate, 9a

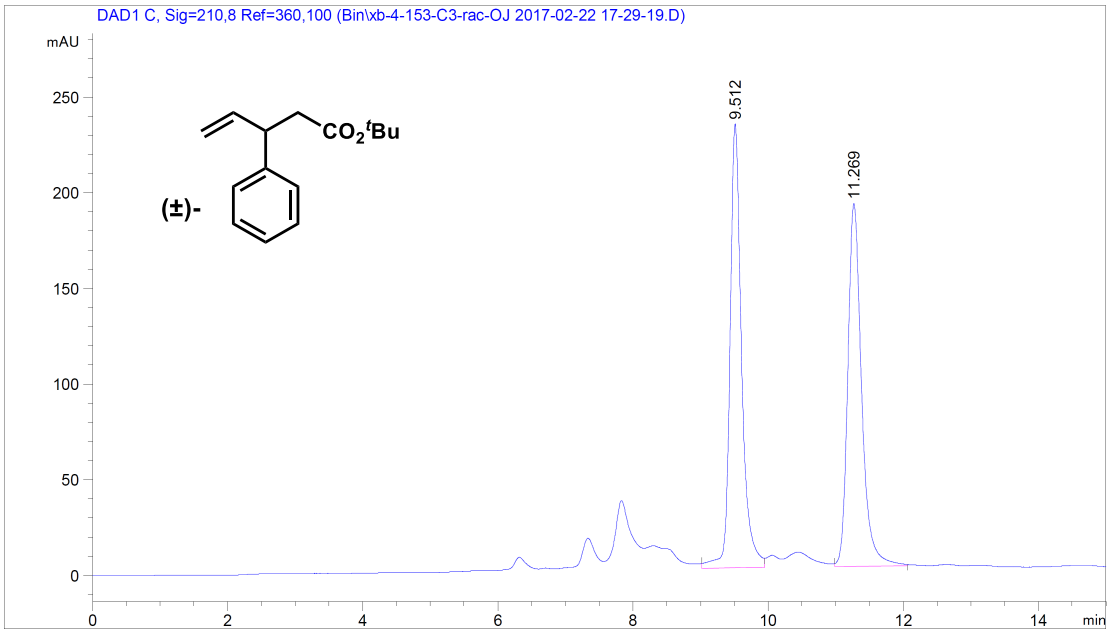


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	6.742	BB	0.1495	2566.97363	50.6589	?
2	7.643	BB	0.1640	2500.19385	49.3411	?

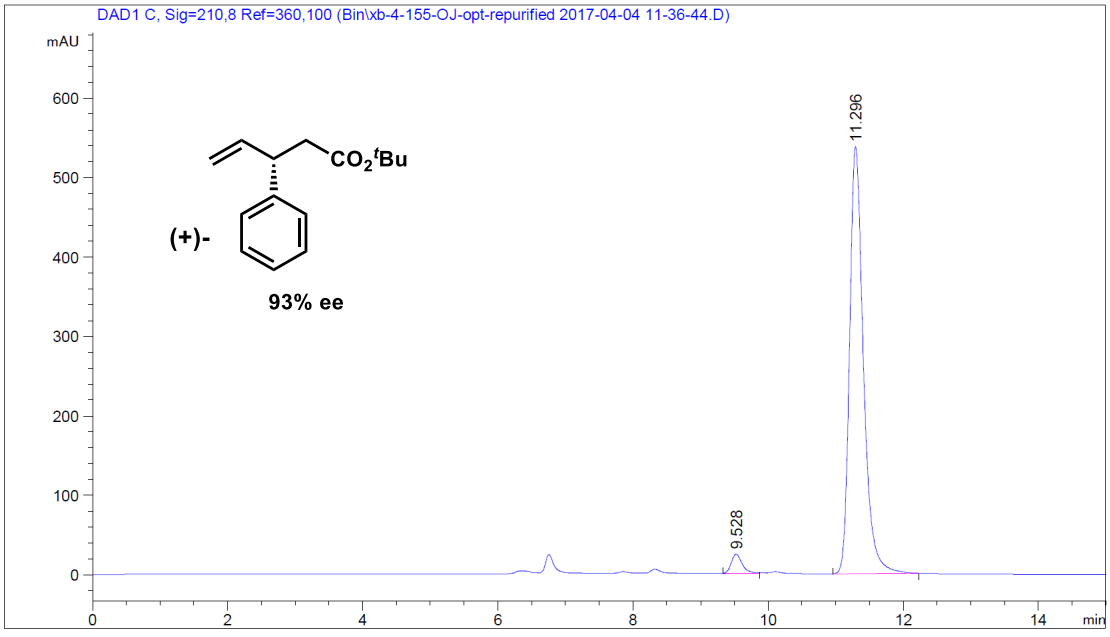


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	6.786	BB	0.1459	3645.92871	98.2371	?
2	7.696	MM	0.1790	65.42645	1.7629	?

(+)-*tert*-Butyl (*S*)-3-phenylpent-4-enoate, 10a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	9.512	BV	0.1774	2771.34204	50.7814	?
2	11.269	BB	0.2132	2686.05420	49.2186	?



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	9.535	BV	0.1733	319.20947	3.5842	?
2	11.298	BB	0.2150	8586.81641	96.4158	?